# Supporting Information

## Silver-Mediated Radical Cascade Trifluoromethylthiolation/Cyclization of Benzimidazole Derivatives with $AgSCF_3$

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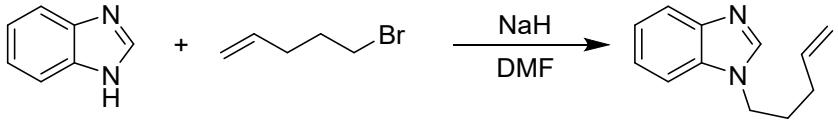
# 1. General Information

All manipulations were performed in dried glass reaction tube equipped with a magnetic stir bar under Ar atmosphere. Solvents and reagents were purchased from commercial sources and used as received. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63 μm, standard grade). Products were purified by flash chromatography on silica gel (200-300 mesh). All NMR spectra were obtained on Bruker AVANCE III systems using $CDCl_3$ as solvent, TMS as internal standard substance, at 400 MHz for $^1H$ NMR, 100 MHz for $^{13}C$ NMR, and 376 MHz for $^{19}F$ NMR. The chemical shifts (δ) are reported in ppm relative to tetramethylsilane. The multiplicities of signals are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quarter), m (multiplet), dd (doublet and doublet). The mass spectra were indicated by GC-MS (Thermo Fisher Scientific ISQ). High-resolution mass spectrometry (HRMS) data were obtained on an Agilent Technologies 1290-6530 UHPLC/Accurate-Mass Quadrupole Time-of Flight (Q-TOF) LC/MS using ESI as ion source. Measured values are reported to 4 decimal places of the calculated value. X-ray analysis was performed with a single-crystal X-ray diffractometer (Gemini E). Melting points were measured with a SGW X-4A microscopic melting point apparatus and were uncorrected. An oil bath is used as heat source for reactions that require heating. Magnetic hot plate stirrer (MS-H-Pro+ ) was purchased from DLAB Scientific Co., Ltd. The material of the reaction vessel (Schlenk tubes) is borosilicate glass.

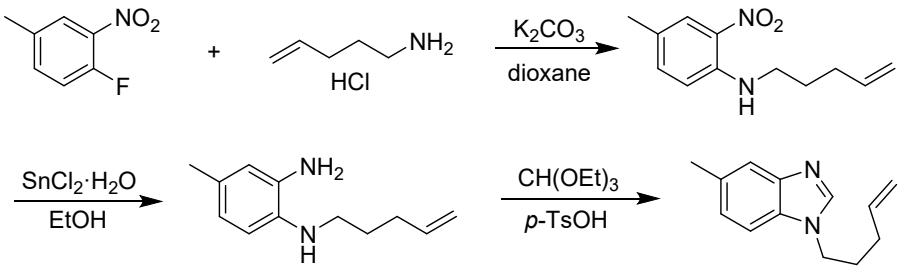
# 2. Substrates Preparation

**Procedure A[1]:**




A dried 100 mL round bottom flask equipped with a magnetic stir bar was charged with 1*H*-benzo[*d*]imidazole (10 mmol, 1.0 equiv.) and DMF (25 mL). After cooling to 0 °C, NaH (12 mmol, 1.2 equiv.) was added and stirring was continued for 30 min at 0 °C. Subsequently, 5-bromopent-1-ene (15 mmol, 1.5 equiv.) in DMF was added to the reaction mixture. The reaction mixture was stirred at room temperature for 2-6 h. After the starting materials completely disappeared (monitored by thin layer chromatography), the reaction mixture was washed with water and extracted with ethyl acetate three times. The combined organic layer was washed with saturated NaCl solution, dried with anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc) to afford co rresponding products (70% yield).

**procedure B[2]:**

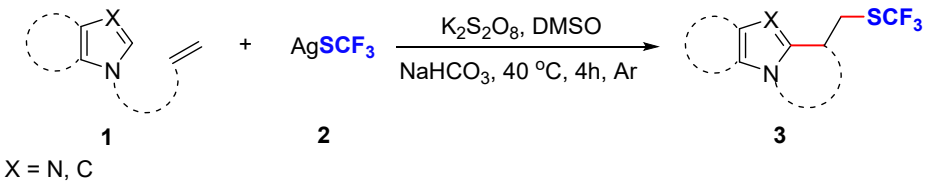



A dried 50 mL round bottom flask equipped with a magnetic stir bar was charged with 1-fluoro-4-methyl-2-nitrobenzene (5.0 mmol, 1.0 equiv.), Pent-4-en-1-amine hydrochloride (6 mmol，1.2 equiv.), $K_2CO_3$ (12.5 mmol, 2.5 equiv.), and 1,4-dioxane (20 mL). After stirring for 10 h at 105 °C under Ar atmosphere. The solution was poured into $H_2O$ (30 mL) and the resulting mixture was extracted with EtOAc (3 × 20 mL). The organic layers were combined and dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo to obtain 4-methyl-2-nitro-N-(pent-4-en-1-yl)aniline. The crude product is used in the next step without further purification.

A dried 50 mL round bottom flask equipped with a magnetic stir bar was charged with 4-methyl-2-nitro-N-(pent-4-en-1-yl)aniline (5mmol, 1.0 equiv.), $SnCl_2$•$2H_2O$ (20 mmol, 4.0 equiv.), and ethanol (20 mL). Subsequently, the resulting mixture was stirred at 90 °C for 5 h under vigorous stirring. After cooling down to room temperature, the reaction mixture was adjusted with 1 M NaOH to pH 7-8, then filtered with diatomite. The filtrate was diluted with EtOAc (30 mL) and successively washed with $H_2O$ (30 mL) and brine (30 mL). Organic layers were combined, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo to afford 4-methyl-$N^1$-(pent-4-en-1-yl)benzene-1,2-diamine without further purification.

A dried 50 mL round bottom flask equipped with a magnetic stir bar was charged with 4-methyl-$N^1$-(pent-4-en-1-yl)benzene-1,2-diamine (5 mmol, 1.0 equiv.), $(EtO)_3CH$ (20 mL). Then, *p*-TsOH (0.4 mmol, 0.1 equiv.) was added and the resulting solution was stirred at room temperature until the reaction was complete (monitored by thin layer chromatography). The solution was diluted with EtOAc, washed with saturated $NaHCO_3$ (3 × 50 mL) and extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography on slica gel (EtOAc/Petroleum ether = 1:1). The pure product 5-methyl-1-(pent-4-en-1-yl)-1H-benzo[d]imidazole was obtained as yellow oil (530 mg, 75% yield of 3 steps).

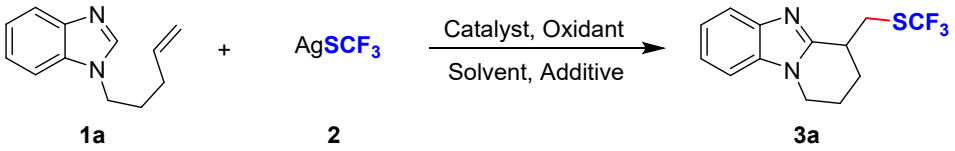
## 3. General procedure for the synthesis of Trifluoromethylthiolated Tricyclic Benzimidazoles




**Experimental Procedure:** A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **1** (0.20 mmol, 1.0 equiv.), **2** (0.30 mmol, 1.5 equiv.), $K_2S_2O_8$ (108.2 mg, 0.4 mmol, 2.0 equiv.), $NaHCO_3$ (20.2 mg, 0.24 mmol, 1.2 equiv.) and DMSO (2.0 mL). The reaction mixture was then stirred at 40 °C for 4 h under Ar atmosphere. The reaction mixture was washed with water and extracted with ethyl acetate three times. The combined organic layer was washed with saturated NaCl solution, dried with anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc) to afford the desired products **3**. The products were characterized by $^1H$ NMR, $^{13}C$ NMR, $^{19}F$ NMR, and HRMS.

## 4. Optimization of the reaction conditions

Table S1. Screening of Solvents[a]

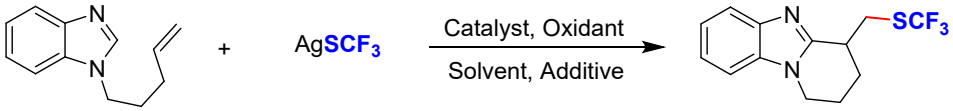



| Entry | Oxidant(equiv.) | Solvent | Additive(equiv.) | Yieldb(%) |
|---|---|---|---|---|
| 1 | $K_2S_2O_8$(2) | $CH_3CN$ | - | 41 |
| 2 | $K_2S_2O_8$(2) | DMAC | - | 42 |
| 3 | $K_2S_2O_8$(2) | DMF | - | 58 |
| 4 | $K_2S_2O_8$(2) | DMSO | - | 68 |
| 5 | $K_2S_2O_8$(2) | MeOH | - | 28 |
| 6 | $K_2S_2O_8$(2) | NMP | - | 22 |
| 7 | $K_2S_2O_8$(2) | DCE | - | trace |

| | | | | |
|---|---|---|---|---|
| 8 | $K_2S_2O_8$(2) | THF | - | NR |
| 9 | $K_2S_2O_8$(2) | dioxane | - | NR |

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2** (0.4mmol, 2.0 equiv.), $K_2S_2O_8$ (0.4mmol, 2.0 equiv.), solvent (2.0 mL), 40 °C, 4 h, Ar. [b]Isolated yield.

Table S2. Screening of Additives[a]

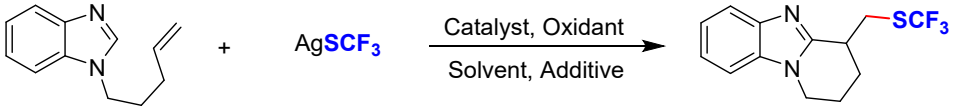



**1a** **2** **3a**

| Entry | Oxidant(equiv.) | Solvent | Additive(equiv.) | Yield[b](%) |
|---|---|---|---|---|
| 1 | $K_2S_2O_8$(2) | DMSO | - | 68 |
| 2 | $K_2S_2O_8$(2) | DMSO | 4-$MeC_6H_4COOH$(2) | 37 |
| 3 | $K_2S_2O_8$(2) | DMSO | TsOH(2) | 42 |
| 4 | $K_2S_2O_8$(2) | DMSO | $H_3PO_3$(2) | 62 |
| 5 | $K_2S_2O_8$(2) | DMSO | $CH_3COOH$(2) | 69 |
| 6 | $K_2S_2O_8$(2) | DMSO | 4-$CF_3C_6H_4COOH$(2) | 70 |
| 7 | $K_2S_2O_8$(2) | DMSO | PivOH(2) | 74 |
| 8 | $K_2S_2O_8$(2) | DMSO | $CF_3COOH$(2) | 75 |
| 9 | $K_2S_2O_8$(2) | DMSO | $NaHCO_3$(2) | 75 |
| 10 | $K_2S_2O_8$(2) | DMSO | $Et_3N$(2) | 69 |
| 11 | $K_2S_2O_8$(2) | DMSO | $K_2HPO_4$(2) | 65 |
| 12 | $K_2S_2O_8$(2) | DMSO | DBU(2) | 48 |
| 13 | $K_2S_2O_8$(2) | DMSO | DABCO(2) | 15 |
| 14 | $K_2S_2O_8$(2) | DMSO | $Cs_2CO_3$(2) | 13 |
| 15 | $K_2S_2O_8$(2) | DMSO | $NaHCO_3$(1.0) | 72 |
| 16 | $K_2S_2O_8$(2) | DMSO | $NaHCO_3$(1.2) | 77 |
| 17 | $K_2S_2O_8$(2) | DMSO | $NaHCO_3$(1.5) | 75 |
| 18[c] | $K_2S_2O_8$(2) | DMSO | $NaHCO_3$(1.2) | 34 |
| 19[d] | $K_2S_2O_8$(2) | DMSO | $NaHCO_3$(1.2) | 56 |

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2** (0.4mmol, 2.0 equiv.), $K_2S_2O_8$ (0.4mmol, 2.0equiv.), additive, DMSO (2.0 mL), 40 °C, 4 h, Ar. [b]Isolated yield. [c]$O_2$. [d]Air.

Table S3. Screening of Oxidants[a]

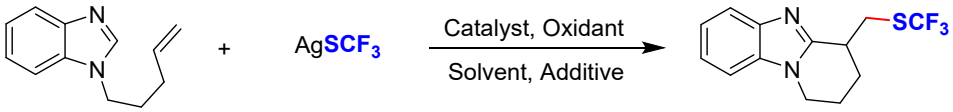



**1a** **2** **3a**

| Entry | Oxidant(equiv.) | Solvent | Additive(equiv.) | Yield[b](%) |
|---|---|---|---|---|
| 1 | $K_2S_2O_8$(2) | DMSO | $NaHCO_3$(1.2) | 77 |
| 2 | $Na_2S_2O_8$(2) | DMSO | $NaHCO_3$(1.2) | 67 |
| 3 | $(NH_4)_2S_2O_8$(2) | DMSO | $NaHCO_3$(1.2) | 47 |
| 4 | TBHP(2) | DMSO | $NaHCO_3$(1.2) | NR |
| 5 | DTBP(2) | DMSO | $NaHCO_3$(1.2) | NR |
| 6 | TEMPO(2) | DMSO | $NaHCO_3$(1.2) | NR |
| 7 | BPO(2) | DMSO | $NaHCO_3$(1.2) | NR |
| 8 | $PhI(OAc)_2$(2) | DMSO | $NaHCO_3$(1.2) | NR |
| 9 | AIBN(2) | DMSO | $NaHCO_3$(1.2) | NR |
| 10 | - | DMSO | $NaHCO_3$(1.2) | NR |
| 11 | PIFA(2) | DMSO | $NaHCO_3$(1.2) | NR |
| 12 | NFSI(2) | DMSO | $NaHCO_3$(1.2) | NR |
| 13 | $K_2S_2O_8$(1.5) | DMSO | $NaHCO_3$(1.2) | 74 |
| 14 | $K_2S_2O_8$(2.5) | DMSO | $NaHCO_3$(1.2) | 68 |

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2** (0.4mmol, 2.0 equiv.), oxidant, $NaHCO_3$ (0.24mmol, 1.2 equiv.), DMSO (2.0 mL), 40 °C, 4 h, Ar. [b]Isolated yield.

Table S4. Screening of Temperature[a]



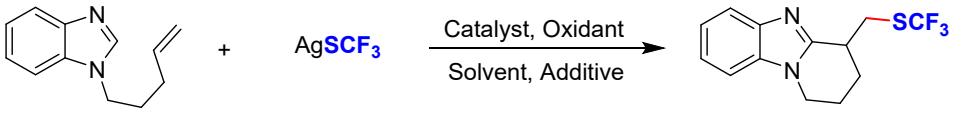

**1a** **2** **3a**

| Entry | Oxidant(equiv.) | Solvent | Tempreture(°C | Additive(equiv. | Yield[b](% |
|---|---|---|---|---|---|
| 1 | $K_2S_2O_8$(2) | DMSO | 27 | $NaHCO_3$(1.2) | 40 |
| 2 | $K_2S_2O_8$(2) | DMSO | 40 | $NaHCO_3$(1.2) | 77 |

| | | | | | |
|---|---|---|---|---|---|
| 3 | $K_2S_2O_8$(2) | DMSO | 50 | $NaHCO_3$(1.2) | 75 |

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2** (0.4mmol, 2.0 equiv.), $K_2S_2O_8$ (0.4mmol, 2.0 equiv.), $NaHCO_3$ (0.24mmol, 1.2 equiv.), DMSO (2.0 mL), temperature (°C), 4 h, Ar. [b]Isolated yield.

Table S5. Screening of Time[a]

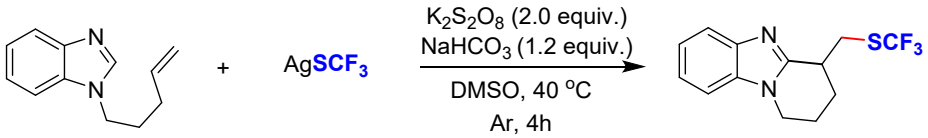



**1a** **2** **3a**

| Entry | Oxidant(equiv.) | Solvent | Time(h) | Additive(equiv. | Yield[b](% |
|---|---|---|---|---|---|
| 1 | $K_2S_2O_8$(2) | DMSO | 2 | $NaHCO_3$(1.2) | 66 |
| 2 | $K_2S_2O_8$(2) | DMSO | 3 | $NaHCO_3$(1.2) | 71 |
| 3 | $K_2S_2O_8$(2) | DMSO | 4 | $NaHCO_3$(1.2) | 77 |
| 4 | $K_2S_2O_8$(2) | DMSO | 6 | $NaHCO_3$(1.2) | 75 |

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2** (0.4mmol, 2.0 equiv.), $K_2S_2O_8$ (0.4mmol, 2.0 equiv.), $NaHCO_3$ (0.24mmol, 1.2 equiv.), DMSO (2.0 mL), 40 °C, time (h), Ar. [b]Isolated yield.

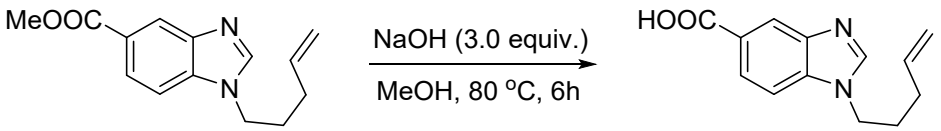
## 5. Scale-up Reaction




**1a** 0.930 g (5 mmol) **2** 1.567 g (4.5 mmol) **3a** 0.975g, (68 %)

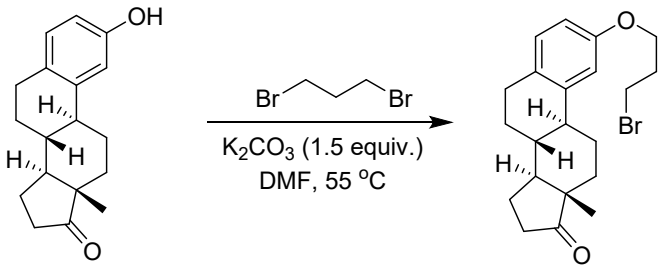
A dried 50 mL round bottom flask equipped with a magnetic stir bar was charged with 1-(pent-4-en-1-yl)-1H-benzo[d]imidazole **1a** (0.930 g, 5.0 mmol, 1.0 equiv.), $AgSCF_3$ **2** (1.567 g, 7.5 mmol, 1.5 equiv.), $K_2S_2O_8$ (2.073 g, 10 mmol, 2.0 equiv.), $NaHCO_3$ (0.504 g, 6 mmol, 1.2 equiv.) and DMSO (30 mL). The reaction mixture was then stirred at 40 °C for 4 h under Ar atmosphere. The reaction mixture was washed with water and extracted with ethyl acetate three times. The combined organic layer was washed with saturated NaCl solution, dried with anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 3:1) to afford the pure product **3a** (0.975 g) in 68% yield.

## 6. Procedure for the synthesis of 7[3]



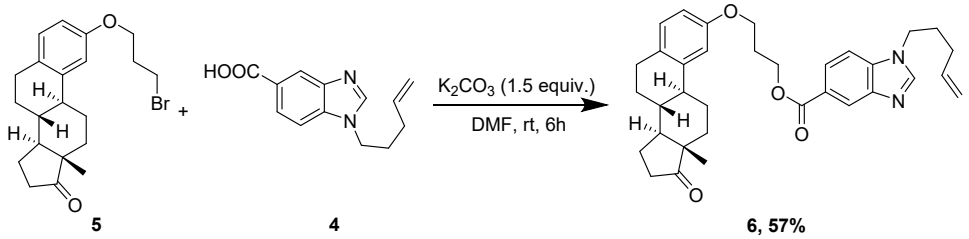

**1i** **4**, (74%)

A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with methyl 1-(pent-4-en-1-yl)-1H-benzo[d]imidazole-5-carboxylate **1i** (0.5 mmol, 1.0 equiv.), NaOH (1.5 mmol, 3.0 equiv.), and $CH_3OH$ (5 mL). The reaction mixture was heated to 80 °C for 6 h. Then, the accomplished reaction was cooled to room temperature. The filtrate was concentrated under vacuo. Then, 1 M HCl was added to the concentrated filtrate until grey solids were precipitated (pH to 4-6). The pure product **4** is afforded in 74 % yield.




***Estrone*** **5**

A dried 50 mL round bottom flask equipped with a magnetic stir bar was charged with estrone (5 mmol, 1,0 equiv.), $K_2CO_3$ (7.5 mmol, 1.5 equiv.) and DMF. The reaction mixture was heated to 55 °C for 10 mins, then 1,3-dibromopropane (7.5 mmol, 1.5 equiv.) was added dropwise to the reaction solution and stirred at 55 °C for 12 h. After cooling down to room temperature, the reaction mixture was washed with water and extracted with ethyl acetate three times. The combined organic layer was washed with saturated NaCl solution. The organic layers were combined, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 5:1) to obtain the desired product **5**.

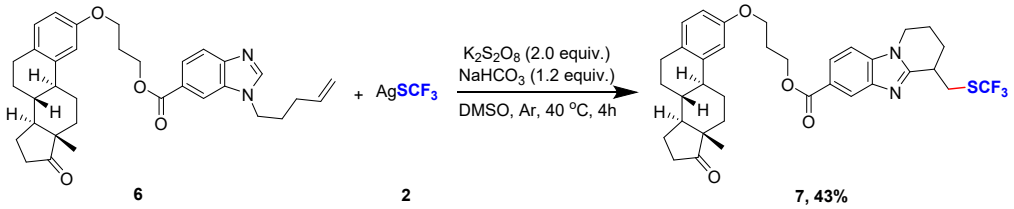



**5** **4** **6, 57%**

from Estrone

A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **4** (0.2 mmol, 1.0 equiv.), brominated estrone **5** (0.3 mmol, 1.5 equiv.), $K_2CO_3$ (0.3 mmol, 1.5 equiv.) and DMF. The reaction mixture was stirred at room temperature for 6 h. Then the reaction mixture was washed with water and extracted with ethyl acetate three

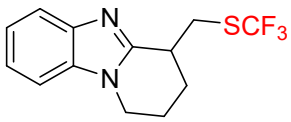
times. The combined organic layer was washed with saturated NaCl solution and dried with anhydrous $Na_2SO_4$ and filtered. The organic layers were combined, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 3:1) to obtain the desired product **6 (**colorless liquid, 61.7 mg, 57% yield).




**6** **2** **7, 43%**

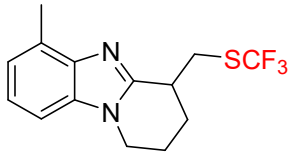
A dried 50 mL round bottom flask equipped with a magnetic stir bar was charged with compound **6** (54.1 mg, 0.1 mmol, 1.0 equiv.), $AgSCF_3$ **2** (31.2 mg, 0.15 mmol, 1.5 equiv.), $K_2S_2O_8$ (54.1 mg, 0.2 mmol, 2.0 equiv.), $NaHCO_3$ (10.1 mg, 0.12 mmol, 1.2 equiv.) and DMSO (1 mL). The reaction mixture was then stirred at 40 °C for 4 h under Ar atmosphere. The reaction mixture was washed with water and extracted with ethyl acetate three times. The combined organic layer was washed with saturated NaCl solution and dried with anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 3:1) to afford the desired product **7 (**white solid, 27.8 mg, in 43% yield).

## 6. Characterization data of products 3



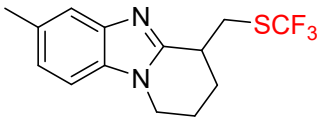

**4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine**

White solid, 77% yield (44.1 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). M.p. = 77.2-78.9 °C. **$^1$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.74-7.72 (m, 1 H), 7.29-7.27 (m, 1 H), 7.27-7.22 (m, 2 H), 4.19-4.14 (m, 1 H), 3.97-3.90 (m, 1 H), 3.83 (dd, $J$ = 3.4 Hz, 1.0 Hz, 1 H), 3.39-3.32 (m, 1 H), 3.26-3.20 (m, 1 H), 2.39-2.32 (m, 1 H), 2.30-2.24 (m, 1 H), 2.11-2.00 (m, 1 H), 1.73-1.82 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 152.2, 142.7, 134.6, 131.1 (q, $J$ = 304.5 Hz), 122.5, 122.4, 119.4, 109.2, 42.5, 36.4, 33.0 (q, $J$ = 1.9 Hz), 25.7, 21.5; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.02. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{14}F_3N_2S$ 287.0824; Found 287.0822.



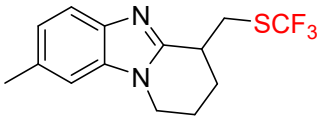
**5-methyl-4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine**

White solid, 58% yield (34.8 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). M.p. = 67.0-69.4 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.18-7.12 (m, 2 H), 7.08-7.06 (m, 1 H), 4.19-4.13 (m, 1 H), 4.00-3.93 (m, 1 H), 3.85 (dd, *J* = 3.3 Hz, 1.0 Hz, 1 H), 3.44-3.37 (m, 1 H), 3.30-3.24 (m, 1 H), 2.66 (s, 3 H), 2.38-2.24 (m, 2 H), 2.02-2.13 (m, 1 H), 1.88-1.79 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 151.4, 142.1, 134.3, 131.2 (q, *J* = 304.1 Hz), 129.5, 122.9, 122.3, 106.6, 42.6, 36.2, 33.3 (q, *J* = 1.6 Hz), 25.7, 21.4, 16.8; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.00. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{14}H_{16}F_3N_2S$ 301.0981; Found 301.0979.



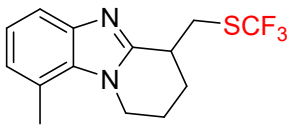

**6-methyl-4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine**

White solid, 74% yield (44.1 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). M.p. = 114.0-116.0 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7. 7.51 (s, 1 H), 7.17 (d, *J* = 2.0 Hz, 1 H), 7.08 (dd, *J* = 2.0 Hz, *J* = 0.2 Hz, 1 H), 4.19-4.14 (m, 1 H), 3.98-3.91 (m, 1 H), 3.82 (dd, *J* = 3.4 Hz, *J* = 1.0 Hz, 1 H), 3.39-3.32 (m, 1 H), 3.27-3.21 (m, 1 H), 2.47 (s, 3 H), 2.37-2.25 (m, 2 H), 2.13-2.02 (m, 1 H), 1.84-1.74 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 152.1, 143.0, 132.7, 132.2, 131.2 (q, *J* = 304.2 Hz), 123.9, 119.2, 108.7, 42.5, 36.3, 33.1 (q, *J* = 1.7 Hz), 25.7, 21.7, 21.5; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.01. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{14}H_{16}F_3N_2S$ 301.0981; Found 301.0982.



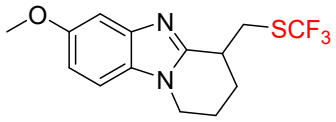

**7-methyl-4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine**

White solid, 68% yield (40.9 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). M.p. = 57.2-59.1 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.60 (d, *J* = 2.1 Hz, 1 H), 7.09-7.07 (m, 2 H), 4.17-4.12 (m, 1 H), 3.95-3.89 (m, 1 H), 3.82 (dd, *J* = 3.4 Hz, 1.0 Hz, 1 H), 3.38-3.31 (m, 1 H), 3.25-3.20 (m, 1 H), 2.49 (s, 3 H), 2.39-2.24 (m, 2 H), 2.12-2.01 (m, 1 H), 1.82-1.73 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 151.7, 140.8, 134.9, 132.4, 131.2 (q, *J* = 304.1 Hz), 124.1, 118.9, 109.2, 42.5, 36.4, 33.1 (q, *J* = 1.9 Hz), 25.8, 21.9, 21.6; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.02. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{14}H_{16}F_3N_2S$ 301.0981; Found 301.0980.



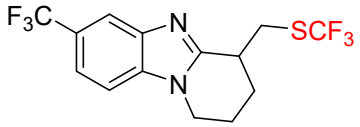

**9-methyl-4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine**

White solid, 62% yield (37.4 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). M.p. = 72.9-74.7 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.55 (d, *J* = 2.0 Hz, 1 H), 7.11 (t, *J* = 1.9 Hz, 1 H), 6.94 (d, *J* = 1.8 Hz, 1 H), 4.64-4.59 (m, 1 H), 4.33-4.27 (m, 1 H), 3.82 (dd, *J* = 3.4 Hz, 1.0 Hz, 1 H), 3.40-3.33 (m, 1 H), 3.28-3.22 (m, 1 H), 2.70 (s, 3 H), 2.36-2.22 (m, 2 H), 2.11-2.01 (m, 1 H), 1.81-1.72 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 152.2, 143.0, 133.6, 131.2 (q, *J* = 304.3 Hz), 124.9, 122.4, 121.4, 117.4, 45.6, 36.7, 33.3 (q, *J* = 1.9 Hz), 25.2, 22.2, 18.8; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.01. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{14}H_{16}F_3N_2S$ 301.0981; Found 301.0982.



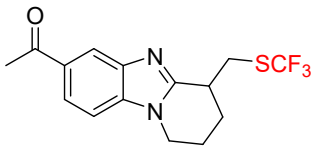

**7-methoxy-4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine**

White solid, 45% yield (28.5 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). M.p. = 97.1-99.6 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.23 (d, *J* = 1.0 Hz, 1 H), 7.17 (d, *J* = 2.2 Hz, 1 H), 6.90 (dd, *J* = 2.2 Hz, 1.0 Hz, 1 H), 4.19-4.13 (m, 1 H), 3.98-3.91 (m, 1 H), 3.84 (s, 3 H), 3.82 (dd, *J* = 3.4 Hz, 1.0 Hz, 1 H), 3.39-3.32 (m, 1 H), 3.26-3.20 (m, 1 H), 2.40-2.24 (m, 2 H), 2.13-2.02 (m, 1 H), 1.83-1.73 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 156.5, 152.4, 143.5, 131.2 (q, *J* = 304.2 Hz), 129.3, 112.4, 109.5, 101.8, 55.9, 42.6, 36.4, 33.1 (q, *J* = 2.0 Hz), 25.7, 21.6; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.07. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{14}H_{16}F_3N_2OS$ 317.0930; Found 317.0928.



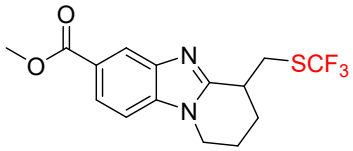

**7-(trifluoromethyl)-4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine**

White solid, 69% yield (49.2 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). M.p. = 86.0-88.2 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.00 (s, 1 H), 7.49 (dd, *J* = 2.1 Hz, 0.3 Hz, 1 H), 7.36 (d, *J* = 2.1 Hz, 1 H), 4.26-4.21 (m, 1 H), 4.04-3.97 (m, 1 H), 3.79 (dd, *J* = 3.4 Hz, 1.0 Hz, 1 H), 3.44-3.37 (m, 1 H), 3.30-3.24 (m, 1 H), 2.43-2.30 (m, 2 H), 2.17-2.06 (m, 1 H), 1.87-1.78 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 154.4, 142.3, 136.7, 131.1 (q, *J* = 304.5 Hz), 125.1 (q, *J* = 32.0 Hz), 125.0 (q, *J* = 270.3 Hz), 119.4 (q, *J* = 3.6 Hz), 117.1 (q, *J* = 4.0 Hz), 109.6, 42.8, 36.6, 32.9 (q, *J* = 2.0 Hz), 25.6, 21.5; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.12, -60.63. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{14}H_{13}F_6N_2S$ 355.0698; Found 355.0697.



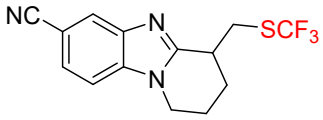
**1-(4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridin-7-yl)ethan-1-one**

White solid, 72% yield (47.3 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 1:1). M.p. = 109.0-112.0 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.34 (d, *J* = 0.3 Hz, 1 H), 7.95 (dd, *J* = 2.1 Hz, 0.4 Hz, 1 H), 7.33 (d, *J* = 2.1 Hz, 1 H), 4.28-4.23 (m, 1 H), 4.05-3.98 (m, 1 H), 3.81 (dd, *J* = 3.4 Hz, 1.0 Hz, 1 H), 3.44-3.37 (m, 1 H), 3.30-3.24 (m, 1 H), 2.65 (s, 3 H), 2.44-2.30 (m, 2 H), 2.17-2.06 (m, 1 H), 1.87-1.78 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 198.0, 154.3, 142.3, 137.9, 132.4, 131.1 (q, *J* = 304.2 Hz), 122.8, 121.1, 109.2, 42.9, 36.7, 32.9 (q, *J* = 2.0 Hz), 26.8, 25.6, 21.5; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.11. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{15}H_{16}F_3N_2OS$ 329.0930; Found 329.0932.



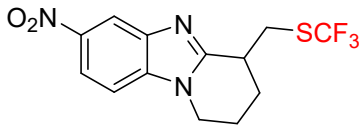

**Methyl-4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine-7-carboxylate**

White solid, 72% yield (49.5 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 1:1). M.p. = 73.2-75.0 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.45 (d, *J* = 0.3 Hz, 1 H), 7.99 (dd, *J* = 2.1 Hz, 0.4 Hz, 1 H), 7.31 (d, *J* = 2.1 Hz, 1 H), 4.27-4.22 (m, 1 H), 4.05-3.98 (m, 1 H), 3.94 (s, 3 H), 3.83 (dd, *J* = 3.4 Hz, 1.0 Hz, 1 H), 3.44-3.37 (m, 1 H), 3.30-3.24 (m, 1 H), 2.44-2.29 (m, 2 H), 2.17-2.06 (m, 1 H), 1.88-1.78 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 167.7, 154.1, 142.3, 137.9, 131.1 (q, *J* = 304.2 Hz), 124.9, 124.2, 121.8, 108.9, 52.2, 42.9, 36.6, 32.9 (q, *J* = 1.6 Hz), 25.6, 21.5; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.05. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{15}H_{16}F_3N_2OS$ 345.0879; Found 345.0880.



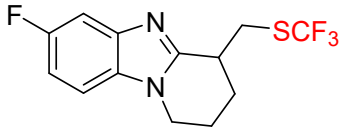

**4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine-7-carbonitrile**

White solid, 71% yield (44.2 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 1:1). M.p. = 98.4-101.0 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.00 (d, *J* = 0.2 Hz, 1 H), 7.49 (dd, *J* = 2.1 Hz, 0.4 Hz, 1 H), 7.36 (dd, *J* = 2.1 Hz, 0.1 Hz, 1 H), 4.28-4.23 (m, 1 H), 4.06-3.99 (m, 1 H), 3.79 (dd, *J* = 3.4 Hz, 1.0 Hz, 1 H), 3.45-3.38 (m, 1 H), 3.30-3.24 (m, 1 H), 2.45-2.31 (m, 2 H), 2.18-2.07 (m, 1 H), 1.88-1.79 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 155.1, 142.4, 137.4, 131.0 (q, *J* = 304.3 Hz), 126.0, 124.4, 120.0, 110.3, 105.8, 42.9, 36.6, 32.8 (q, *J* = 2.0 Hz), 25.5, 21.4; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.08. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{14}H_{13}F_3N_3S$ 312.0777; Found 312.0775.



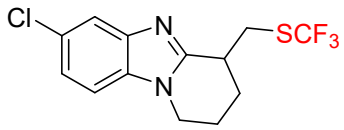
**7-nitro-4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine**

White solid, 74% yield (49.1 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 1:1). M.p. = 147.7-149.8 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.53 (d, *J* = 0.5 Hz, 1 H), 8.12 (dd, *J* = 2.2 Hz, 0.5 Hz, 1 H), 7.32 (d, *J* = 2.2 Hz, 1 H), 4.30-4.25 (m, 1 H), 4.08-4.01 (m, 1 H), 3.80 (dd, *J* = 3.4 Hz, 1.0 Hz, 1 H), 3.45-3.38 (m, 1 H), 3.31-3.25 (m, 1 H), 2.46-2.33 (m, 2 H), 2.20-2.11 (m, 1 H), 1.89-1.80 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 156.2, 143.9, 142.1, 138.8, 131.0 (q, *J* = 304.2 Hz), 118.3, 116.0, 109.1, 43.1, 36.8, 32.7 (q, *J* = 1.8 Hz), 25.4, 21.4; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.09. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{13}H_{13}F_3N_3O_2S$ 332.0675; Found 332.0637.



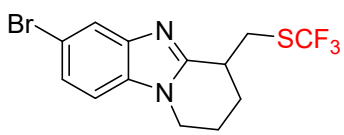

**7-fluoro-4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine**

White solid, 70% yield (42.6 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 1:1). M.p. = 51.6-53.4 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.38 (dd, *J* = 2.4 Hz, 0.6 Hz, 1 H), 7.20-7.17 (m, 1 H), 7.01-6.96 (m, 1 H), 4.19-4.14 (m, 1 H), 3.99-3.92 (m, 1 H), 3.79 (dd, *J* = 3.4 Hz, 1.0 Hz, 1 H), 3.39-3.32 (m, 1 H), 3.26-3.20 (m, 1 H), 2.39-2.26 (m, 2 H), 2.13-2.03 (m, 1 H), 1.84-1.75 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 159.6 (d, *J* = 235.6 Hz), 153.7, 143.1 (d, *J* = 12.7 Hz), 131.2, 131.1 (q, *J* = 304.2 Hz), 110.7 (d, *J* = 25.9 Hz), 109.5 (d, *J* = 10.4 Hz), 105.3 (d, *J* = 24.1 Hz), 42.6, 36.5, 32.9 (q, *J* = 2.0 Hz), 25.5, 21.5; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.06, -120.63. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{13}H_{13}F_4N_2S$ 305.0730; Found 305.0732.



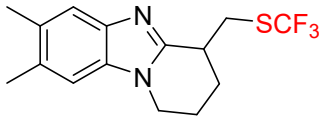

**7-chloro-4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine**

White solid, 70% yield (44.6 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 1:1). M.p. = 72.3-74.1 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.69-7.68 (m, 1 H), 7.22-7.17 (m, 2 H), 4.19-4.14 (m, 1 H), 3.99-3.92 (m, 1 H), 3.78 (dd, *J* = 3.4 Hz, 1.0 Hz, 1 H), 3.40-3.33 (m, 1 H), 3.26-3.21 (m, 1 H), 2.40-2.26 (m, 2 H), 2.14-2.03 (m, 1 H), 1.84-1.75 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 153.5, 143.6, 133.3, 131.1 (q, *J* = 304.5 Hz), 128.1, 122.9, 119.3, 110.0, 42.7, 36.5, 32.9 (q, *J* = 1.9 Hz), 25.6, 21.5; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.05. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{13}H_{13}ClF_3N_2S$ 321.0435; Found 321.0434.



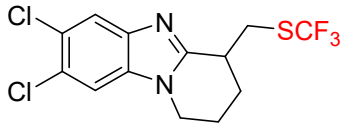
**7-bromo-4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine**

White solid, 65% yield (47.4 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 1:1). M.p. = 73.5-75.7 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.85 (d, *J* = 0.4 Hz, 1 H), 7.33 (dd, *J* = 2.1 Hz, 0.4 Hz, 1 H), 7.14 (d, *J* = 2.1 Hz, 1 H), 4.19-4.14 (m, 1 H), 3.98-3.92 (m, 1 H), 3.78 (dd, *J* = 3.4 Hz, 1.0 Hz, 1 H), 3.40-3.33 (m, 1 H), 3.26-3.21 (m, 1 H), 2.41-2.27 (m, 2 H), 2.14-2.03 (m, 1 H), 1.85-1.75 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 153.4, 144.1, 133.6, 131.1 (q, *J* = 304.2 Hz), 125.5, 122.3, 115.5, 110.4, 42.7, 36.5, 32.9 (q, *J* = 1.7 Hz), 25.6, 21.5; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.05. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{13}H_{13}BrF_3N_2S$ 364.9929; Found 364.9931.



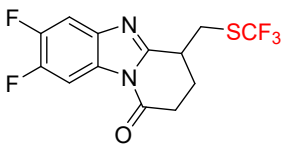

**7,8-dimethyl-4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine**

White solid, 62% yield (38.8 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). M.p. = 147.5-149.6 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.48 (s, 1 H), 7.06 (s, 1 H), 4.16-4.11 (m, 1 H), 3.95-3.88 (m, 1 H), 3.81 (dd, *J* = 3.4 Hz, 1.0 Hz, 1 H), 3.38-3.31 (m, 1 H), 3.26-3.20 (m, 1 H), 2.38 (s, 3 H), 2.36 (s, 3 H), 2.34-2.30 (m, 1 H), 2.30-2.23 (m, 1 H), 2,11-2.00 (m, 1 H), 1.82-1.73 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 151.3, 141.3, 133.2, 131.6, 131.3, 131.2 (q, *J* = 304.2 Hz), 119.5, 109.5, 42.5, 36.4, 33.2 (q, *J* = 1.9 Hz), 25.8, 21.6, 20.6, 20.4; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.01. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{15}H_{18}F_3N_2S$ 315.1137; Found 315.1137.



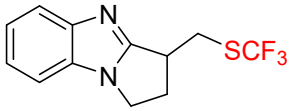

**7,8-dichloro-4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine**

White solid, 71% yield (56.0 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). M.p. = 125.6-127.9 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.77 (s, 1 H), 7.36 (s, 1 H), 4.17-4.12 (m, 1 H), 3.97-3.90 (m, 1 H), 3.77 (dd, *J* = 3.4 Hz, 1.0 Hz, 1 H), 3.40-3.21 (m, 2 H), 2.42-2.35 (m, 1 H), 2.35-2.28 (m, 1 H), 2,15-2.04 (m, 1 H), 1.85-1.76 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 154.4, 142.1, 133.9, 131.0 (q, *J* = 304.0 Hz), 126.5, 126.4, 120.6, 110.7, 42.8, 36.6, 32.8 (q, *J* = 1.8 Hz), 25.5, 21.4; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.08. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{13}H_{12}Cl_2F_3N_2S$ 355.0045; Found 355.0046.



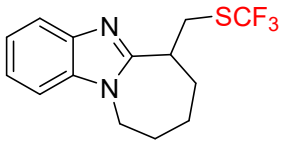
**7,8-difluoro-4-(((trifluoromethyl)thio)methyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-a]pyridin-1(2H)-one**

White solid, 42% yield (28.9 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). M.p. = 110.5-113.0 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.04 (dd, *J* = 2.5 Hz, 1.8 Hz, 1 H), 7.48 (dd, *J* = 2.5 Hz, 1.8 Hz, 1 H), 3.81 (dd, *J* = 3.5 Hz, 1.1 Hz, 1 H), 3.46-3.39 (m, 1 H), 3.30-3.25 (m, 1 H), 3.06-3.00 (m, 1 H), 2.93-2.84 (m, 1 H), 2.54-2.47 (m, 1 H), 2.15-2.04 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 167.9, 155.8 (d, *J* = 3.5 Hz), 150.5 (dd, *J* = 14.3 Hz, 6.5 Hz), 148.1 (dd, *J* = 14.1 Hz, 6.7 Hz), 138.0 (dd, *J* = 10.2 Hz, 2.1 Hz), 130.9 (q, *J* = 304.6 Hz), 126.7 (dd, *J* = 11.2 Hz, 1.4 Hz), 107.7 (d, *J* = 20.4 Hz), 104.2 (d, *J* = 24.3 Hz), 36.6, 32.9, 31.3 (q, *J* = 2.1 Hz), 25.5; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.22, -138.58 (d, *J* = 5.4 Hz), -138.72 (d, J = 5.4 Hz). **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{13}H_{10}F_5N_2OS$ 337.0429; Found 337.0433.



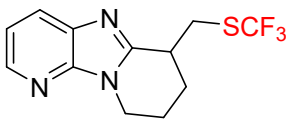

**3-(((trifluoromethyl)thio)methyl)-2,3-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole**

White solid, 15% yield (8.1 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 2:1). M.p. = 61.0-63.2 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.75-7.71 (m, 1 H), 7.34-7.30 (m, 1 H), 7.27-7.23 (m, 2 H), 4.23-4.18 (m, 1 H), 4.12-4.05 (m, 1 H), 3.70-3.63 (m, 2 H), 3.16-3.10 (m, 1 H), 3.06-2.98 (m, 1 H), 2.59-2.50 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 160.4, 148.6, 132.3, 130.9 (q, *J* = 304.3 Hz), 122.6, 122.3, 120.2, 109.9, 41.9, 36.2, 32.7 (q, *J* = 2.1 Hz), 32.6; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.77. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{12}H_{12}F_3N_2S$ 273.0668; Found 273.0668.



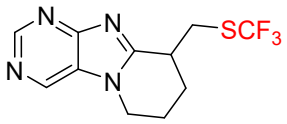

**6-(((trifluoromethyl)thio)methyl)-7,8,9,10-tetrahydro-6H-benzo[4,5]imidazo[1,2-a]azepine**

White solid, 26% yield (15.7 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 101.5-103.2 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.75-7.72 (m, 1 H), 7.30-7.21 (m, 3 H), 4.45-4.40 (m, 1 H), 3.95-3.88 (m, 1 H), 3.80 (dd, *J* = 4.1 Hz, *J* = 1.7 Hz, 1 H), 3.29-3.23 (m, 2 H), 2.21-2.06 (m, 3 H), 1.89-1.82 (m, 1 H), 1.57-1.45 (m, 2 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 157.0, 142.0, 135.7, 131.5 (q, *J* = 304.2 Hz), 122.5, 121.9, 119.7, 108.9, 44.1, 41.2, 32.7 (q, *J* = 2.0 Hz), 31.4, 29.8, 28.3; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -40.88. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{14}H_{16}F_3N_2S$ 301.0981; Found 301.0979.



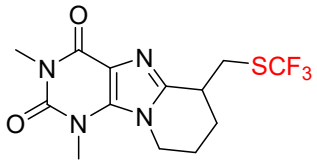
**6-(((trifluoromethyl)thio)methyl)-6,7,8,9-tetrahydroimidazo[1,2-a:5,4-b']dipyridine**

White solid, 47% yield (27.1 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 1:1). M.p. = 144.3-146.5 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.35 (dd, *J* = 1.2 Hz, 0.3 Hz, 1 H), 8.00 (dd, *J* = 2.0 Hz, 0.4 Hz, 1 H), 7.23 (dd, *J* = 2.0 Hz, 1.2 Hz, 1 H), 4.48-4.43 (m, 1 H), 4.10-4.03 (m, 1 H), 3.82 (dd, *J* = 3.4 Hz, 1.0 Hz, 1 H), 3.45-3.38 (m, 1 H), 3.30-3.24 (m, 1 H), 2.45-2.30 (m, 2 H), 2.15-2.04 (m, 1 H), 1.89-1.79 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 153.7, 147.7, 143.7, 135.0, 131.1 (q, *J* = 304.2 Hz), 126.9, 118.7, 41.7, 36.8, 32.8 (q, *J* = 2.0 Hz), 25.7, 21.4; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.10. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{12}H_{13}F_3N_3S$ 288.0777; Found 288.0779.



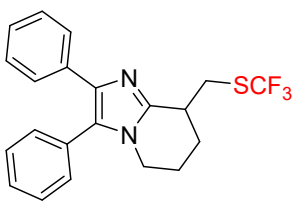

**9-(((trifluoromethyl)thio)methyl)-6,7,8,9-tetrahydropyrido[2,1-f]purine**

White solid, 48% yield (27.8 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 1:1). M.p. = 120.5-123.0 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 9.06 (s, 1 H), 8.94 (s, 1 H), 4.48-4.43 (m, 1 H), 4.09-4.02 (m, 1 H), 3.80 (dd, *J* = 3.4 Hz, 1.0 Hz, 1 H), 3.47-3.39 (m, 1 H), 3.32-3.26 (m, 1 H), 2.48-2.33 (m, 2 H), 2.17-2.05 (m, 1 H), 1.90-1.81 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 155.3, 152.2, 152.1, 147.3, 133.7, 131.0 (q, *J* = 304.2 Hz), 41.9, 37.9, 32.6 (q, *J* = 2.1 Hz), 25.6, 21.3; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.14. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{11}H_{12}F_3N_4S$ 289.0729; Found 289.0728.



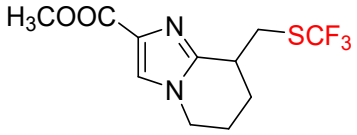

**1,3-dimethyl-6-(((trifluoromethyl)thio)methyl)-6,7,8,9-tetrahydropyrido[1,2-e]purine-2,4(1H,3H)-dione**

White solid, 48% yield (33.1 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 1:1). M.p. = 188.5-191.3 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 4.54-4.49 (m, 1 H), 4.18-4.10 (m, 1 H ), 3.63 (dd, *J* = 3.3 Hz, 1.0 Hz, 1 H), 3,54 (s, 3 H), 3.37 (s, 3 H), 3.28-3.21 (m, 1 H), 3.18-3.12 (m, 1 H), 2.32-2.17 (m, 2 H), 2.06-1.95 (m, 1 H), 1.79-1.70 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 155.3, 151.8, 150.7, 148.4, 131.0 (q, *J* = 304.5 Hz), 107.1, 45.0, 36.0, 32.8 (q, *J* = 1.8 Hz), 29.9, 29.0, 25.0, 21.2; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.16. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{13}H_{16}F_3N_4O_2S$ 349.0941; Found 349.0939.



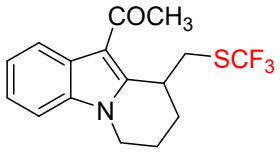
**2,3-diphenyl-8-(((trifluoromethyl)thio)methyl)-5,6,7,8-tetrahydroimidazo[1,2-a]pyridine**

White solid, 26% yield (20.2 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 1:1). M.p. = 128.0-130.2 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.48-7.46 (m, 2 H), 7.45-7.39 (m, 3 H), 7.34-7.32 (m, 2 H), 7.22-7.18 (m, 2 H), 7.15-7.11 (m, 1 H), 3.86 (dd, *J* = 3.3 Hz, 1.0 Hz, 1 H), 3.78-3.72 (m, 1 H), 3.69-3.62 (m, 1 H), 3.34-3.27 (m, 1 H), 3.24-3.18 (m, 1 H), 2.34-2.27 (m, 1 H), 2.14-2.07 (m, 1 H), 1.99-1.88 (m, 1 H), 1.80-1.71 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 145.3, 137.3, 134.7, 131.3 (q, *J* = 304.0 Hz), 131.0, 130.8, 129.1, 128.6, 128.3, 127.9, 127.0, 126.4, 44.0, 35.9, 33.7 (q, *J* = 1.8 Hz), 25.9, 21.9; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.01. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{21}H_{20}F_3N_2S$ 389.1294; Found 389.1291.



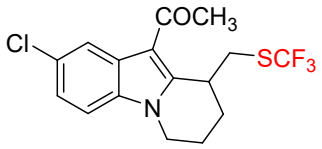

**Methyl-8-(((trifluoromethyl)thio)methyl)-5,6,7,8-tetrahydroimidazo[1,2-a]pyridine-3-carboxylate**

White solid, 65% yield (38.5 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 1:1). M.p. = 91.3-94.0 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.68 (s, 1 H), 4.53-4.74 (m, 1 H), 4.11-4.03 (m, 1 H), 3.82 (s, 3 H), 3.65 (dd, *J* = 3.3 Hz, 1.0 Hz, 1 H), 3.25-3.19 (m, 1 H), 3.16-3.11 (m, 1 H), 2.28-2.14 (m, 2 H), 2.00-1.90 (m, 1 H), 1.74-1.64 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 160.9, 150.5, 136.7, 131.1 (q, *J* = 304.2 Hz), 122.5, 51.5, 45.4, 36.2, 33.1 (q, *J* = 1.6 Hz), 25.0, 21.7; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.21. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{11}H_{14}F_3N_2O_2S$ 295.0723; Found 295.0722.



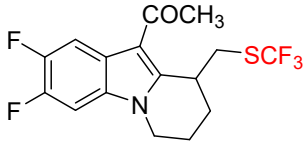

**1-(7-chloro-1-(((trifluoromethyl)thio)methyl)-2,3,4,4a-tetrahydro-1H-fluoren-9-yl)ethan-1-one**

White solid, 58% yield (38.0 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). M.p. = 97.3-99.5 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.93-7.91 (m, 1 H), 7.37-7.27 (m, 3 H), 4.35-4.30 (m, 1 H), 4.05-4.00 (m, 1 H), 3.95-3.88 (m, 1 H), 3.71-3.67 (m, 1 H), 2.96-2.89 (m, 1 H), 2.72 (s, 3 H), 2.42-2.37 (m, 1 H), 2.16-2.10 (m, 2 H), 1.95-1.86 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 194.0, 146.2, 136.3, 131.2 (q, *J* = 304.1 Hz), 126.2, 122.7, 122.5, 120.7, 113.2, 110.0, 42.7, 33.3, 32.0 (q, *J* = 1.7 Hz), 31.7, 22.1, 17.6; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -40.55. **HRMS (ESI-TOF)** *m/z*: [M + H] $^{+}$ Calcd for $C_{16}H_{17}F_3NOS$ 328.0977; Found 328.0977.



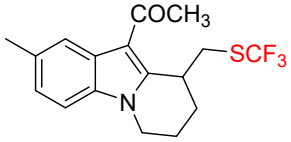
**1-(2-chloro-9-(((trifluoromethyl)thio)methyl)-6,7,8,9-tetrahydropyrido[1,2-a]indol-10-yl)ethan-1-one**

White solid, 73% yield (52.5 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). M.p. = 140.4-142.7 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.85 (d, *J* = 0.3 Hz, 1 H), 7.27-7.21 (m, 2 H), 4.30-4.25 (m, 1 H), 4.02-3.96 (m, 1 H), 3.93-3.86 (m, 1 H), 3.66-3.62 (m, 1 H), 2.94-2.88 (m, 1 H), 2.66 (s, 3 H), 2.40-2.36 (m, 1 H), 2.15-2.09 (m, 2 H), 1.93-1.84 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 193.5, 147.3, 134.7, 131.1 (q, *J* = 304.2 Hz), 128.7, 127.2, 122.7, 120.3, 112.9, 110.9, 42.9, 33.3, 31.9 (q, *J* = 1.2 Hz), 31.6, 21.9, 17.5; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -40.56. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{16}ClF_3NOS$ 362.0588; Found 362.0591.



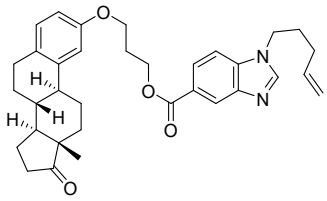

**1-(2,3-difluoro-9-(((trifluoromethyl)thio)methyl)-6,7,8,9-tetrahydropyrido[1,2-a]indol-10-yl)ethan-1-one**

White solid, 81% yield (58.9 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). M.p. = 117.2-119.5 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.66-7.61 (m, 1 H), 7.14-7.09 (m, 1 H), 4.23-4.18 (m, 1 H), 4.00-3.94 (m, 1 H), 3.90-3.82 (m, 1 H), 3.64-3.60 (m, 1 H), 2.95-2.89 (m, 1 H), 2.63 (s, 3 H), 2.41-2.35 (m, 1 H), 2.16-2.09 (m, 2 H), 1.93-1.84 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 193.2, 149.1 (dd, *J* = 13.9 Hz, *J* = 10.8 Hz), 147.3 (d, *J* = 2.5 Hz), 146.9-146.6 (m), 131.5 (d, *J* = 9.3 Hz), 131.1 (q, *J* = 304.4 Hz), 121.5 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz), 113.3 (d, *J* = 3.62 Hz), 108.0 (d, *J* = 20.7 Hz), 98.3 (d, *J* = 21.1 Hz), 43.0, 33.4, 31.9 (q, *J* = 1.1 Hz), 31.4, 21.9, 17.5; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -40.59, -142.30 (d, *J* = 5.5 Hz), -143.26 (d, *J* = 5.5 Hz). **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{15}F_5NOS$ 364.0789; Found 364.0793.



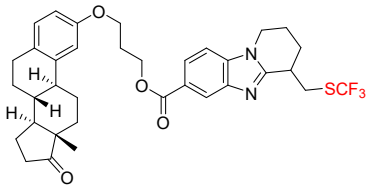

**1-(2-methyl-9-(((trifluoromethyl)thio)methyl)-6,7,8,9-tetrahydropyrido[1,2-a]indol-10-yl)ethan-1-one**

White solid, 46% yield (31.7 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). M.p. = 151.6-153.4 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.69 (s, 1 H), 7.24 (d, *J* = 2.1 Hz, 1 H), 7.12 (dd, *J* = 2.1 Hz, 0.3 Hz, 1 H), 4.31-4.26 (m, 1 H), 4.03-3.97 (m, 1 H), 3.92-3.84 (m, 1 H), 3.70-3.65 (m, 1 H), 2.94-2.88 (m, 1 H), 2.71 (s, 3 H), 2.52 (s, 3 H), 2.40-2.36 (m, 1 H), 2.15-2.08 (m, 2 H), 1.93-1.84 (m, 1 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 194.0, 146.2, 134.7, 132.2, 131.2 (q, *J* = 304.1 Hz), 126.4, 123.9, 120.6, 112.8, 109.6, 42.7, 33.3, 32.0 (q, *J* = 1.2 Hz), 31.8, 22.1, 22.0, 17.6; **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -40.55. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{19}F_3NOS$ 342.1134; Found 342.1133.



**3-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl)oxy)propyl 1-(pent-4-en-1-yl)-1H-benzo[d]imidazole-5-carboxylate**

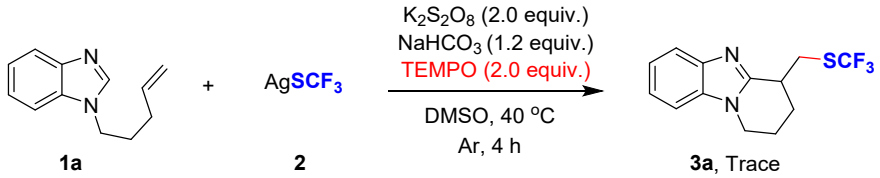
White liquid, 57% yield (61.7 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.04 (d, *J* = 0.2 Hz, 1 H), 7.48 (dd, *J* = 2.1 Hz, 0.4 Hz, 1 H), 7.97 (s, 1 H), 7.41 (d, *J* = 2.1 Hz, 1 H), 7.18 (d, *J* = 2.2 Hz, 1 H), 6.73 (dd, *J* = 2.2 Hz, 0.7 Hz, 1 H), 6.66 (d, *J* = 0.6 Hz, 1 H), 5.83-5.73 (m, 1 H), 5.08 (s, 1 H), 5.05-5.04 (m, 1 H), 4.54 (t, 2 H), 4.20 (t, 2 H), 4.15-4.10 (m, 2 H), 2.90-2.86 (m, 2 H), 2.52-2.46 (m, 1 H), 2.41-2.36 (m, 1 H), 2.29-2.21 (m, 3 H), 2.17-2.12 (m, 1 H), 2.10-2.04 (m, 4 H), 2.02-1.92 (m, 4 H), 1.59-1.39 (m, 5 H), 0.90 (s, 3 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 221.1, 167.1, 156.9, 144.8, 143.6, 137.9, 137.1, 136.5, 132.3, 126.5,124.6 (d, *J* = 1.9 Hz), 122.9, 116.6, 114.7, 112.3, 109.5, 64.5, 61.9, 50.5, 48.1, 44.5, 44.1, 38.5, 36.0, 31.7, 30.6, 29.7, 29.0, 28.8, 26.7, 26.0, 21.7, 14.0. **HRMS (ESI-TOF)** *m/z*: [M + H] $^+$ Calcd for $C_{34}H_{41}N_2O_4$ 541.3061; Found 541.3063.



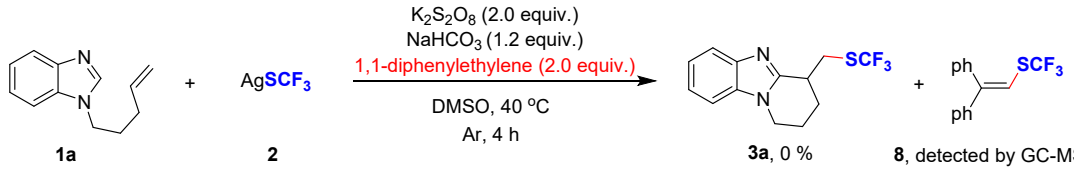
**3-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl)oxy)propyl 4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine-7-carboxylate**

White liquid, 43% yield (27.8 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.45 (d, *J* = 0.2 Hz, 1 H), 8.00 (dd, *J* = 2.1 Hz, 0.4 Hz, 1 H), 7.32 (d, *J* = 2.1 Hz, 1 H), 7.19 (d, *J* = 2.1 Hz, 1 H), 6.73 (dd, *J* = 2.2 Hz, 0.7 Hz, 1 H), 6.66 (d, *J* = 0.7 Hz, 1 H), 4.53 (t, 2 H), 4.28-4.23 (m, 1 H), 4.15-4.11 (m, 2 H), 4,05-3.98 (m, 1 H), 3.82 (dd, *J* = 3.4 Hz, 1.0 Hz, 1 H), 3.45-3.38 (m, 1 H), 3.31-3.12 (m, 1 H), 2.91-2.87 (m, 2 H), 2.53-2.46 (m, 1 H), 2.44-2.36 (m, 2 H), 2.35-2.30 (m, 1 H), 2.28-2.22 (m, 3 H), 2.17-2.09 (m, 2 H), 2.08-2.01 (m 2 H), 2.00-1.93 (m, 2 H), 1.88-1.78 (m, 1 H), 1.56-1.40 (m, 5 H), 0.90 (s, 3 H); **$^{13}$C NMR** (100 MHz, $CDCl_3$, ppm): δ 221.1, 167.1, 157.0, 154.1, 142.3, 137.91, 137.89, 132.3, 131.1 (q, *J* = 304.5 Hz), 126.5, 124.9, 124.3, 121.7, 114.7, 112.3, 109.0, 64.5, 61.8, 50.5, 48.2, 44.1, 42.9, 38.5, 36.6, 36.0, 32.9 (q, *J* = 1.7 Hz), 31.7, 29.8, 29.0, 26.7, 26.0, 25.6, 21.7, 21.5, 14.0. **$^{19}$F NMR** (376 MHz, $CDCl_3$, ppm): δ -41.05. **HRMS (ESI-TOF)** *m/z*: [M + H] $^+$ Calcd for $C_{35}H_{40}F_3N_2O_4S$ 641.2655; Found 641.2659.

## 7. Mechanistic Experiments




A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 1-(pent-4-en-1-yl)-1H-benzo[d]imidazole **1a** (0.20 mmol, 1.0 equiv.), $AgSCF_3$ **2** (0.30 mmol, 1.5 equiv.), $K_2S_2O_8$ (0.4 mmol, 2.0 equiv.), $NaHCO_3$ (0.24 mmol, 1.2 equiv.), TEMPO (0.4 mmol, 2.0 equiv.) and DMSO (2.0 mL). The reaction mixture was then stirred at 40 °C for 4 h under Ar atmosphere. The reaction mixture was washed with water and extracted with ethyl acetate three times. The combined organic layer was washed with saturated NaCl solution, dried with anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated in vacuo. The GC-MS analysis of crude mixture showed that the formation of **3a** was completely inhibited.




A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 1-(pent-4-en-1-yl)-1H-benzo[d]imidazole **1a** (0.20 mmol, 1.0 equiv.), $AgSCF_3$ **2** (0.30 mmol, 1.5 equiv.), $K_2S_2O_8$ (0.4 mmol, 2.0 equiv.), $NaHCO_3$ (0.24 mmol, 1.2 equiv.), 1, 1-diphenylethylene (0.4 mmol, 2.0 equiv.) and DMSO (2.0 mL). The reaction mixture was then stirred at 40 °C for 4 h under Ar atmosphere. The reaction mixture was washed with water and extracted with ethyl acetate three times. The combined organic layer was washed with saturated NaCl solution, dried with anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated in vacuo. The GC-MS analysis of crude mixture showed that the formation of **3a** was totally suppressed. The expected adduct **8** was observed by GC-MS as following: **GC-MS** (m/z, relative intensity): 280 (M +, 87), 211 (99), 178 (66), 165 (27), 152 (15). These results showed that the reaction system proceeded in a free radical way.

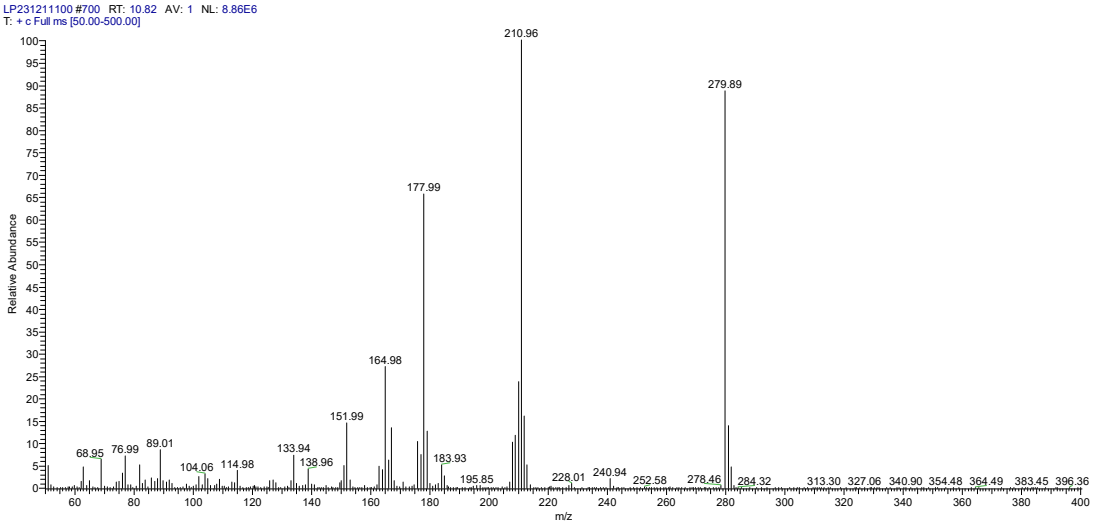



**Figure S1. GC-MS** (m/z) of compound **8**

## 8. X-ray crystallographic data of 3a

The product **3a** was recrystallized from $CDCl_3$. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2360355.

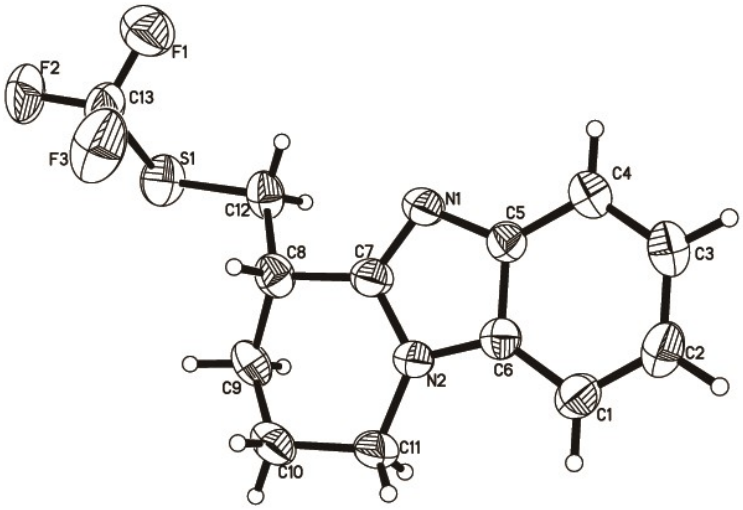



**Figure S2.** X-ray crystal structure of **3a** with the ellipsoid contour at 50% probability Levels.

**Table S6.** Crystal data and structure refinement for **3a**

| | |
|---|---|
| Identification code | **3a** |
| Empirical formula | $C_{13}H_{13}F_3N_2S$ |
| Formula weight | 286.08 |
| Temperature/K | 293(2) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 6.5464(4) |

| | |
|---|---|
| b/Å | 13.7584(8) |
| c/Å | 16.2007(10) |
| α/° | 67.284(6) |
| β/° | 85.636(5) |
| γ/° | 87.696(5) |
| Volume/$Å_3$ | 1341.98(15) |
| Z | 4 |
| ρcalcg/$cm^3$ | 1.417 |
| μ/$mm^{-1}$ | 2.381 |
| F(000) | 592.0 |
| Crystal size/$mm^3$ | 0.17 × 0.11 × 0.04 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 6.966 to 134.156 |

## 9. References


[1] (a) N. Shotaro, S. Takashi, S. Atsushi, K. Tohru, Y. Tsuyoshi and M. Atsunori, Org. Lett., 2012, **14**, 2476-2479; (b) H. G. Huang, M. L. Yu, X. L. Su, P. Guo, J. Zhao, J. B. Zhou and Y. Li, J. Org. Chem., 2018, **83**, 2425-2437.

[2] Y. X. Wang, S. L. Qi, Y. X. Luan, X. W. Han, S. Wang, H. Chen and M. Ye, J. Am. Chem. Soc., 2018, **140**, 5360-5364.

[3] X. Y. Yuan, Y. F. Si, X. Li, S. J. Wu, F. L. Zeng, Q. Y. Lv and B. Yu, Org. Chem. Front., 2022, **9**, 2728-2733.

# 10. Copies of $^{1}$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra

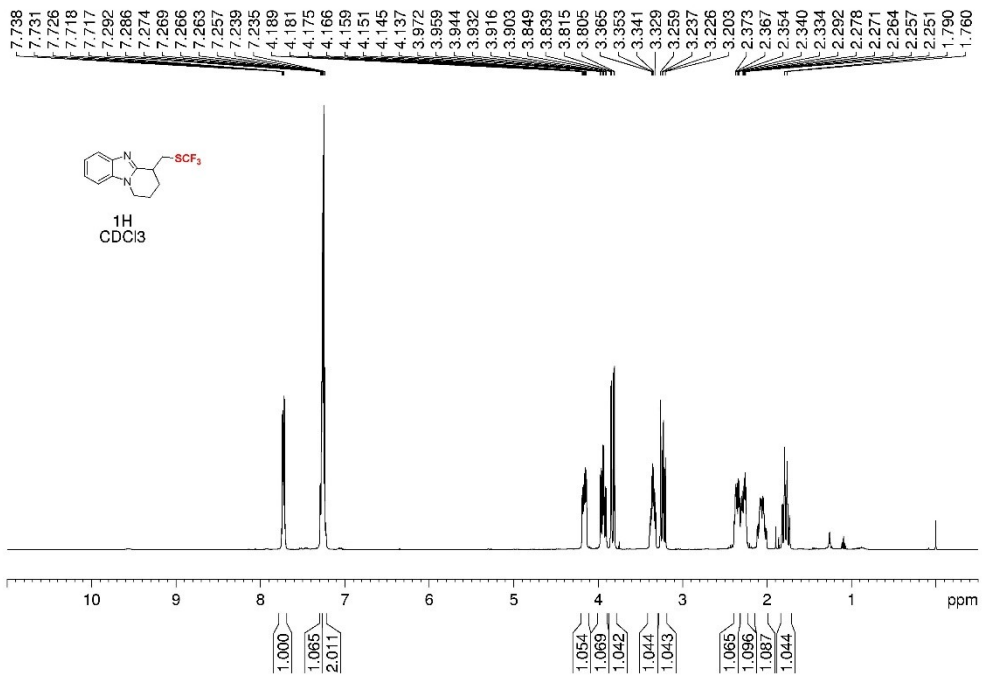



**Figure S3. $^{1}$H NMR (400 MHz, $CDCl_3$) of compound 3a**

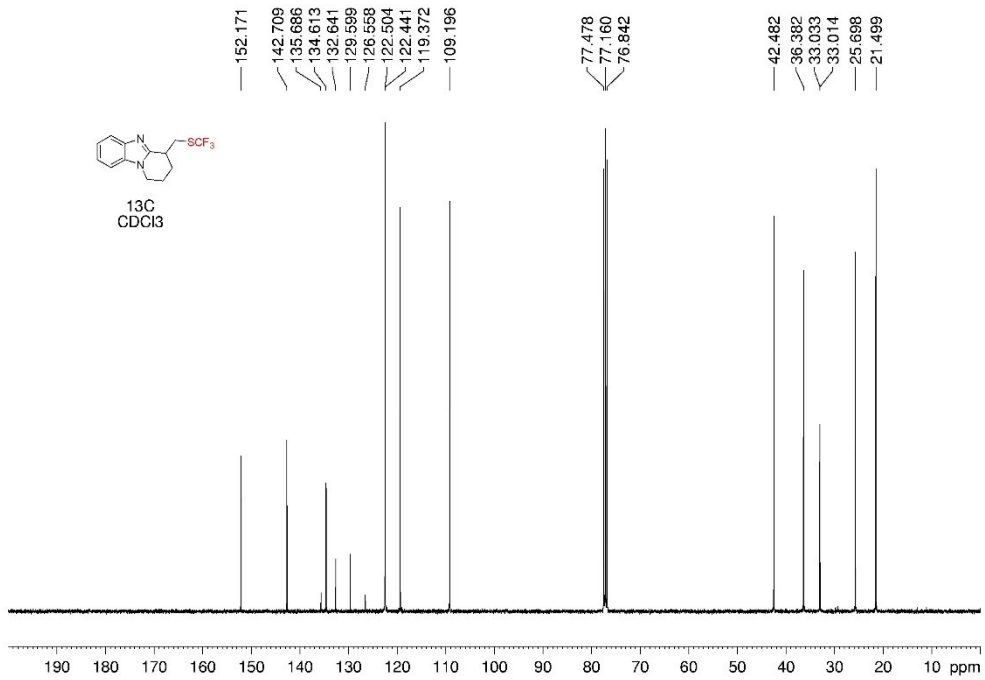



**Figure S4. $^{13}$C NMR (100 MHz, $CDCl_3$) of compound 3a**

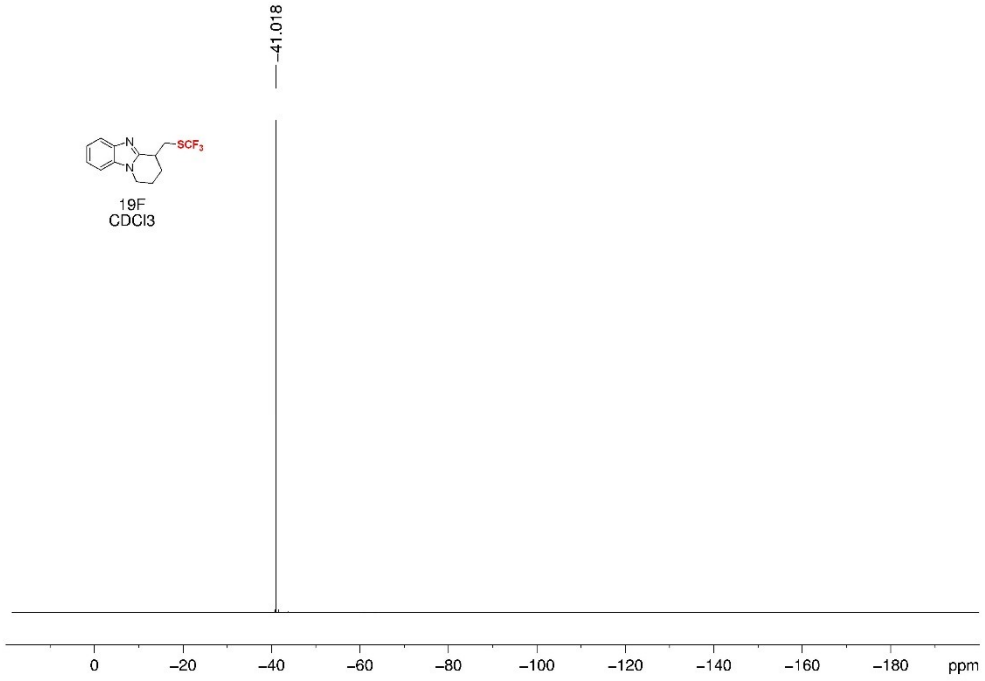



**Figure S5. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3a**

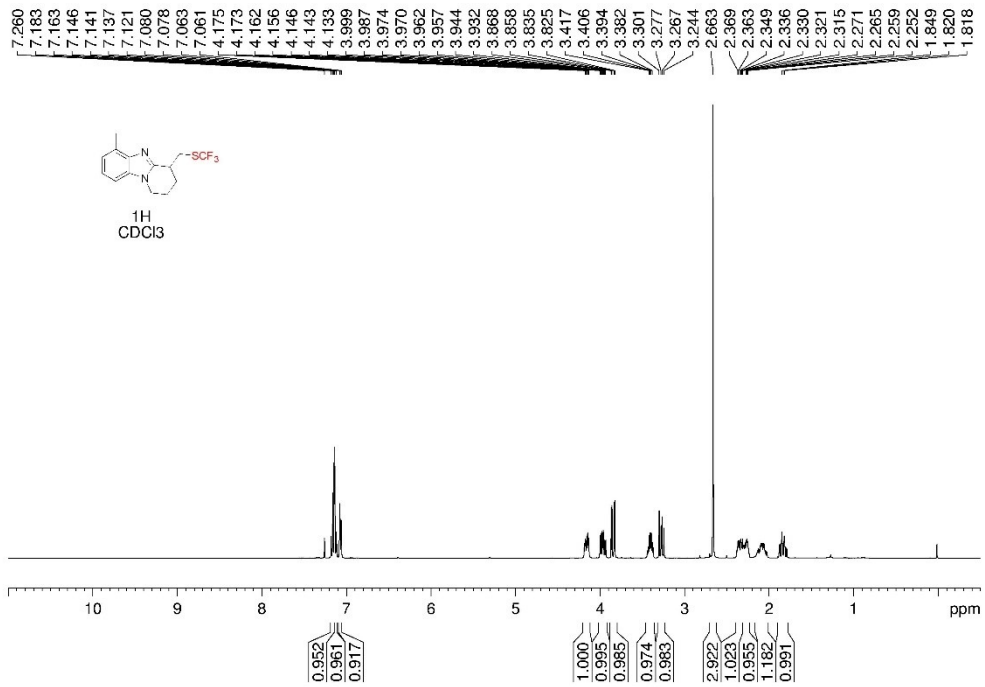



**Figure S6. $^{1}H$ NMR (400 MHz, $CDCl_3$) of compound 3b**

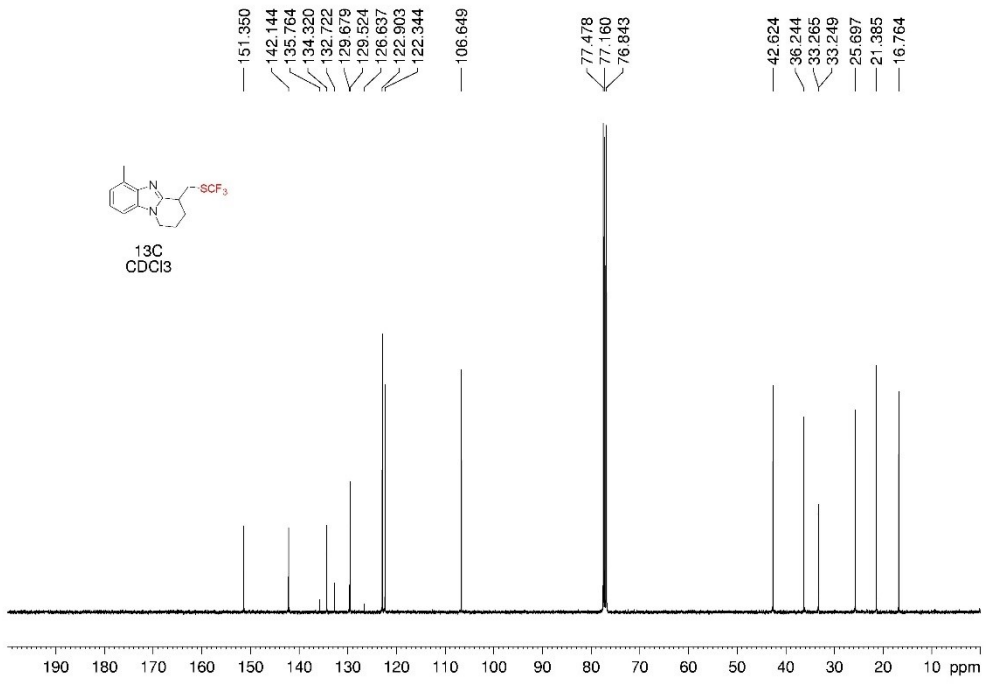



**Figure S7. $^{13}C$ NMR (100 MHz, $CDCl_3$) of compound 3b**

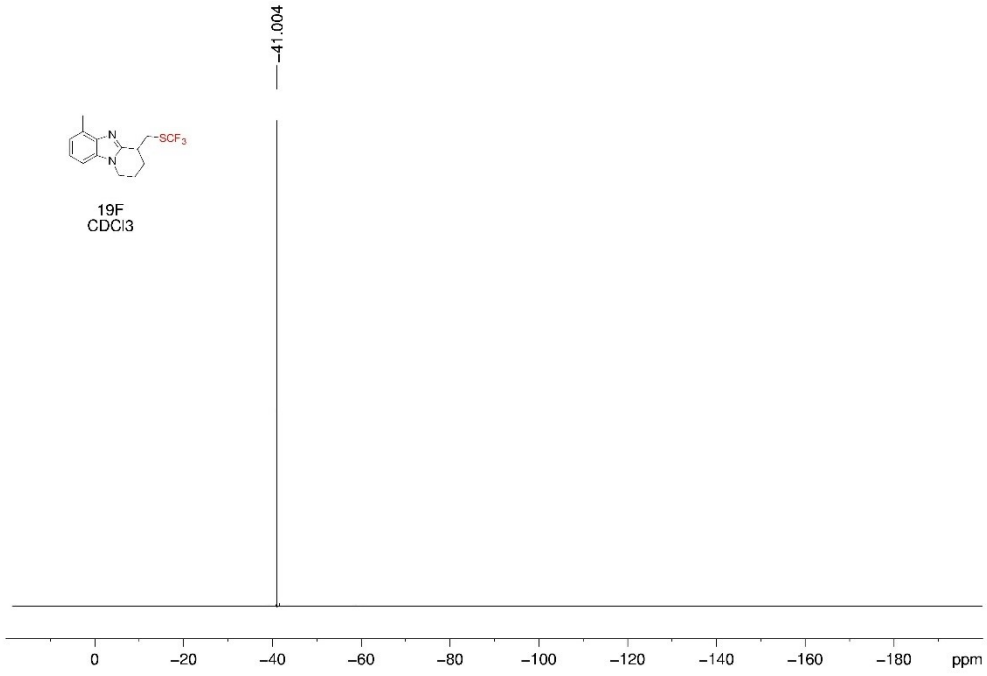



**Figure S8. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3b**

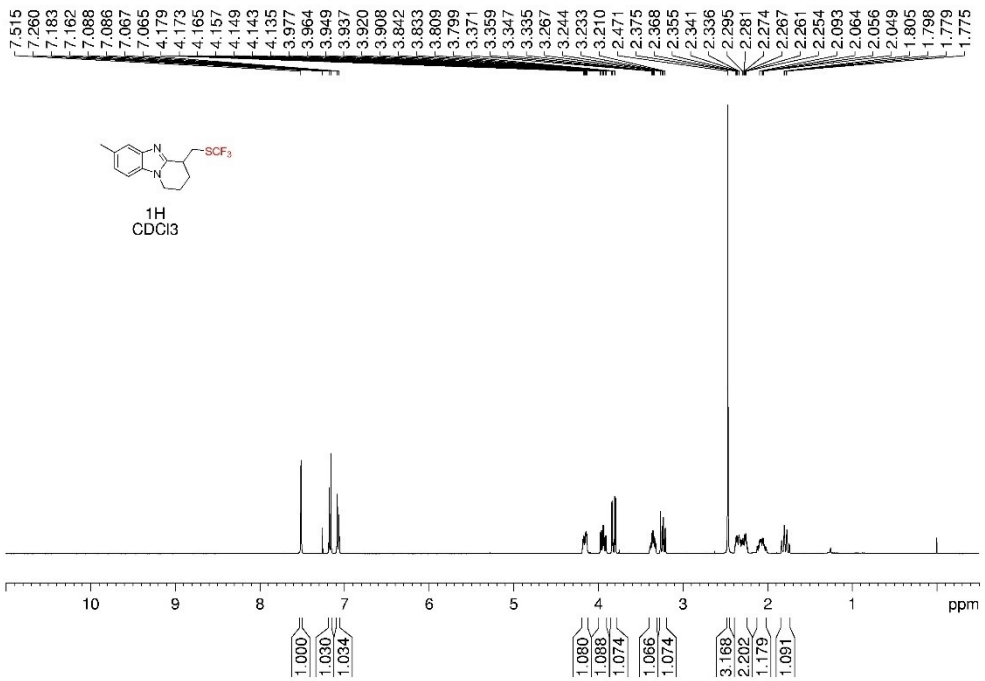



**Figure S9. $^{1}$H NMR (400 MHz, $CDCl_3$) of compound 3c**

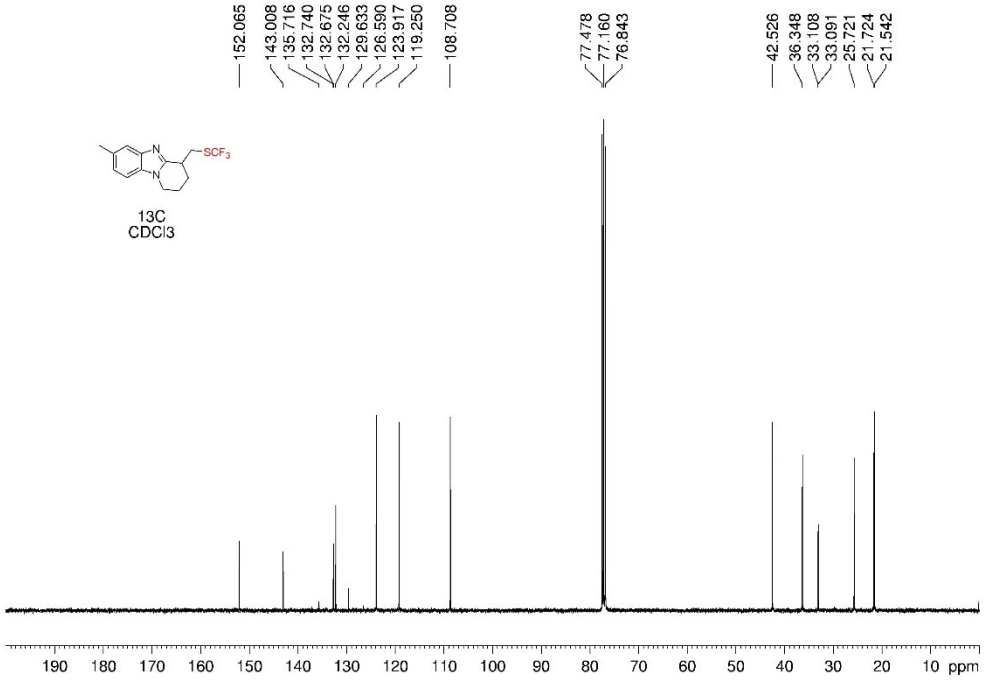



**Figure S10. $^{13}$C NMR (100 MHz, $CDCl_3$) of compound 3c**

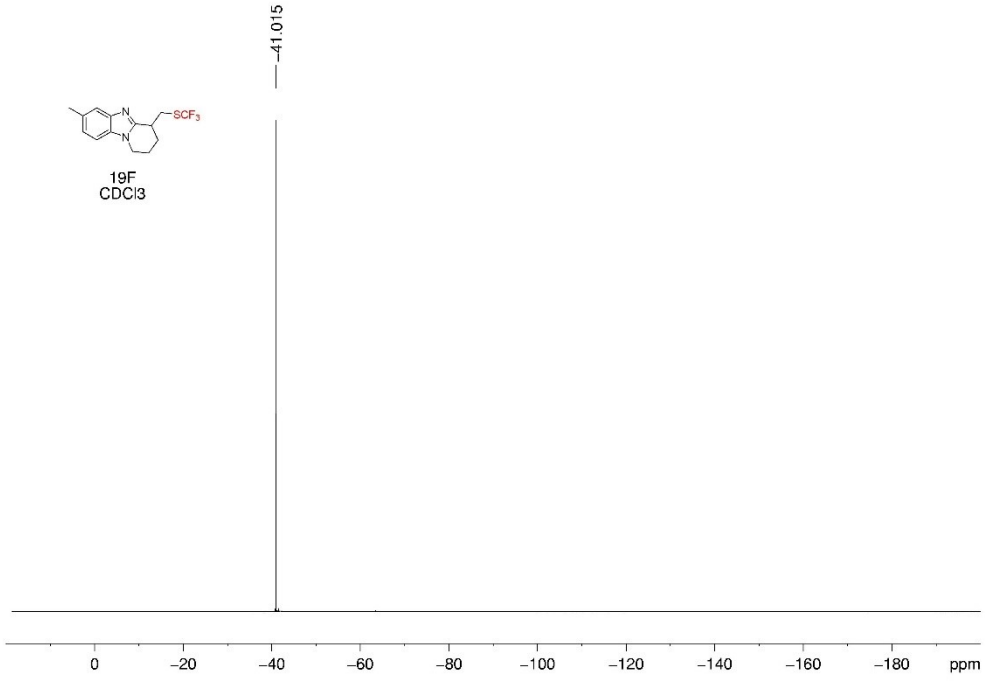



**Figure S11. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3c**

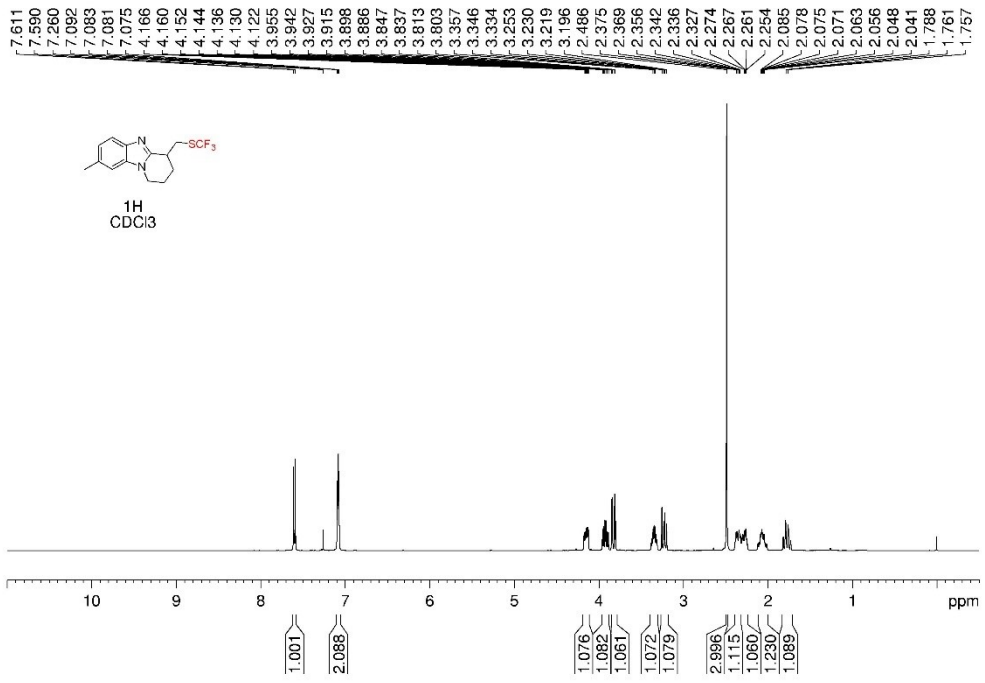



**Figure S12. $^{1}H$ NMR (400 MHz, $CDCl_3$) of compound 3d**

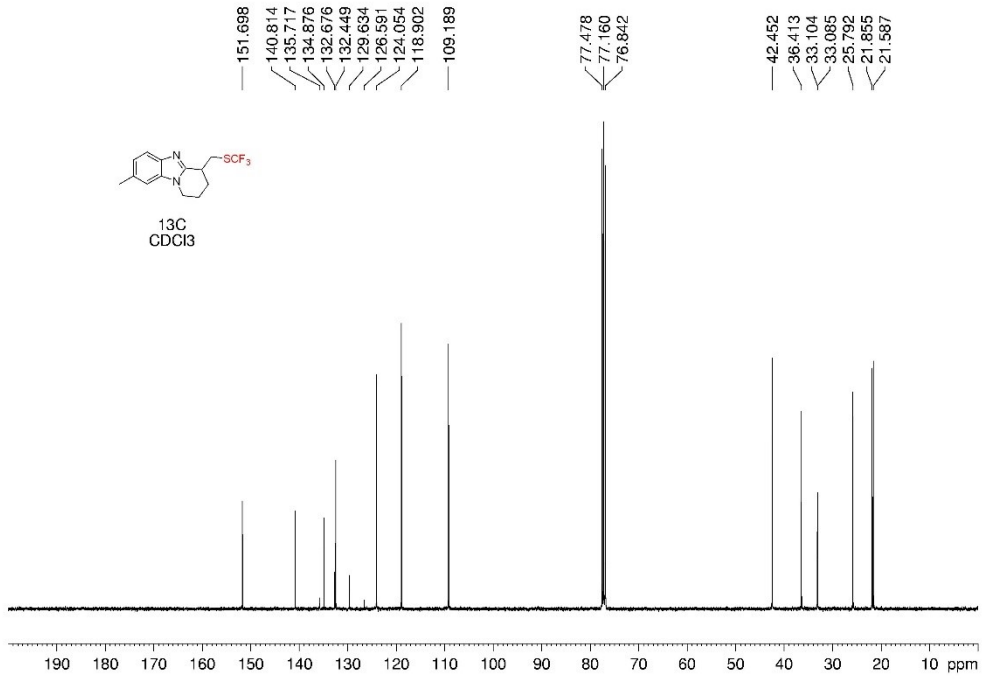



**Figure S13. $^{13}C$ NMR (100 MHz, $CDCl_3$) of compound 3d**

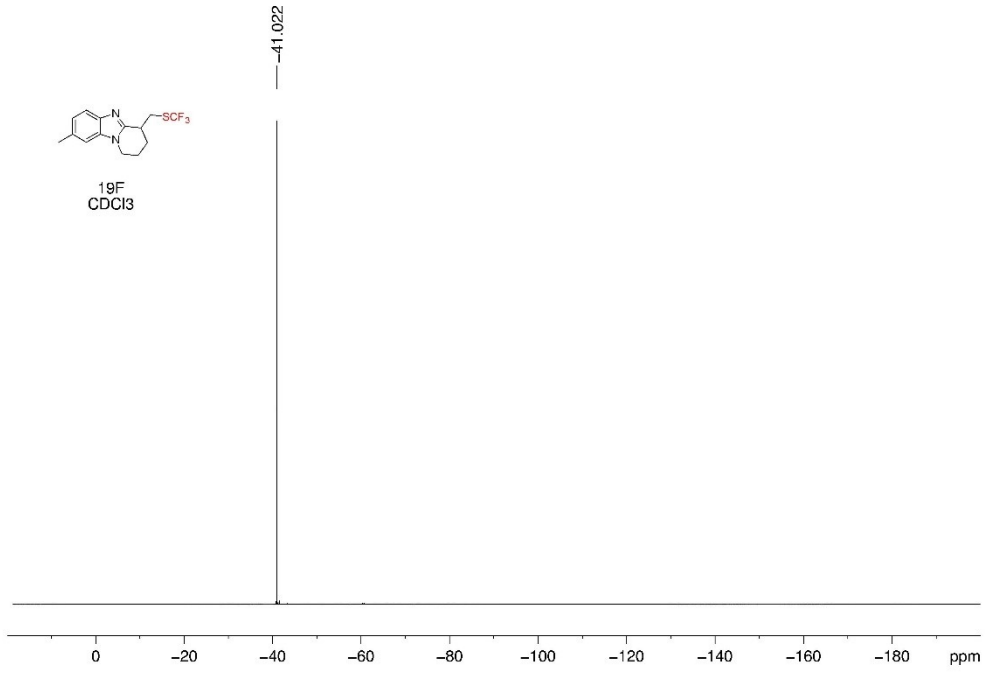



**Figure S14. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3d**

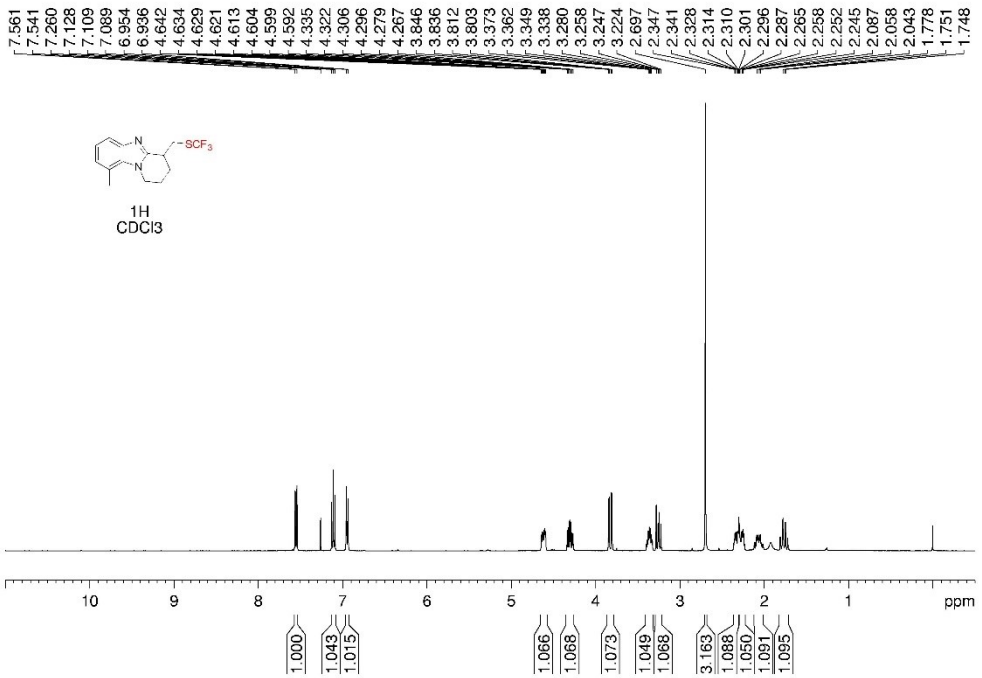



**Figure S5. $^{1}$H NMR (400 MHz, $CDCl_3$) of compound 3e**

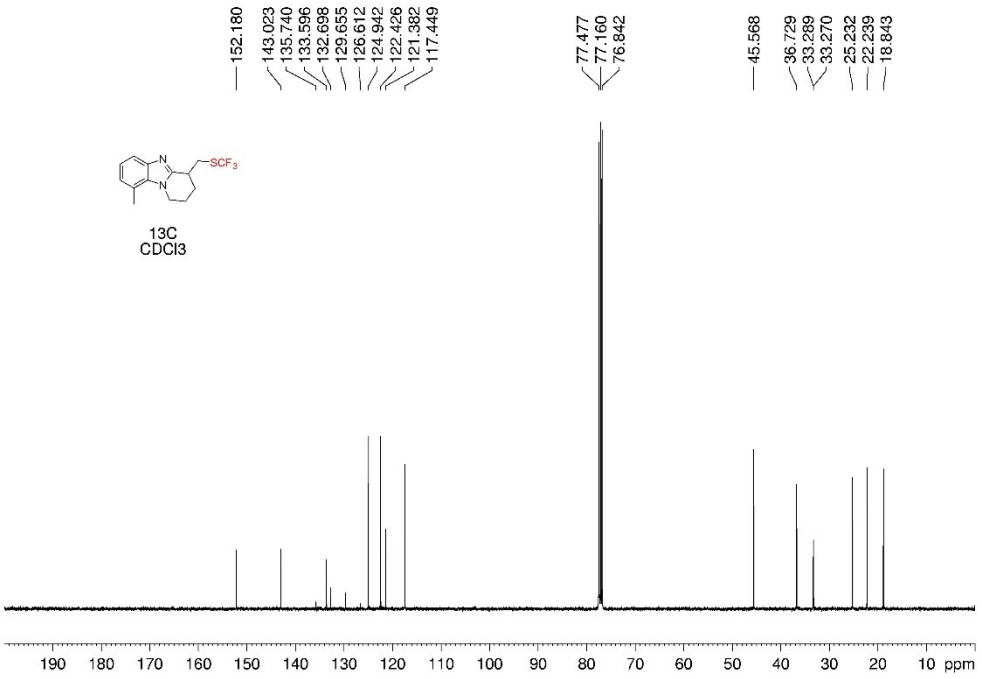



**Figure S16. $^{13}$C NMR (100 MHz, $CDCl_3$) of compound 3e**

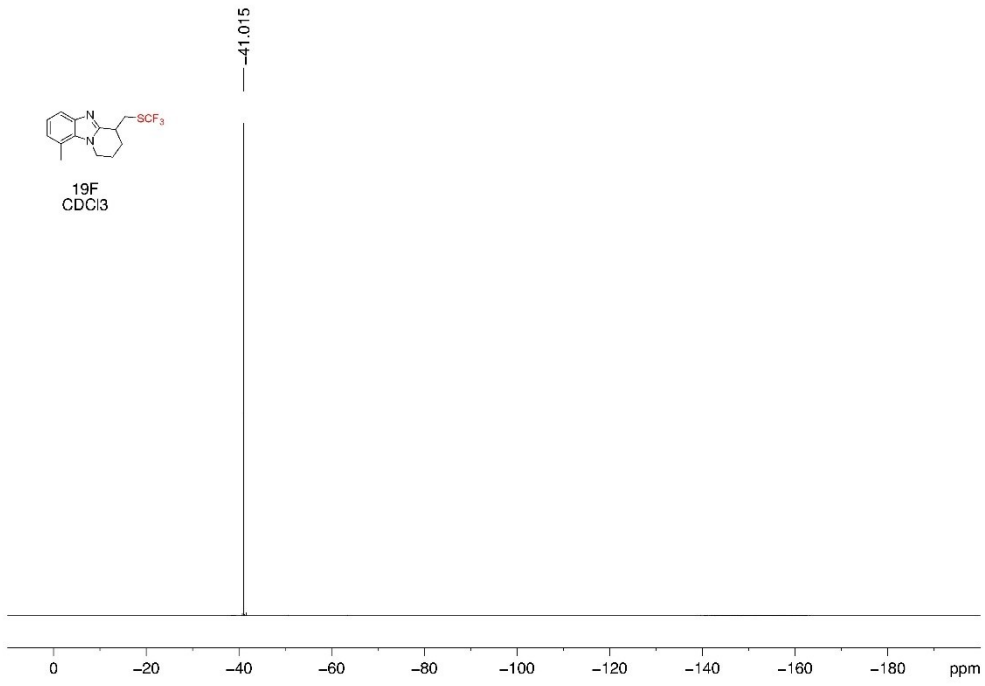



**Figure S17. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3e**

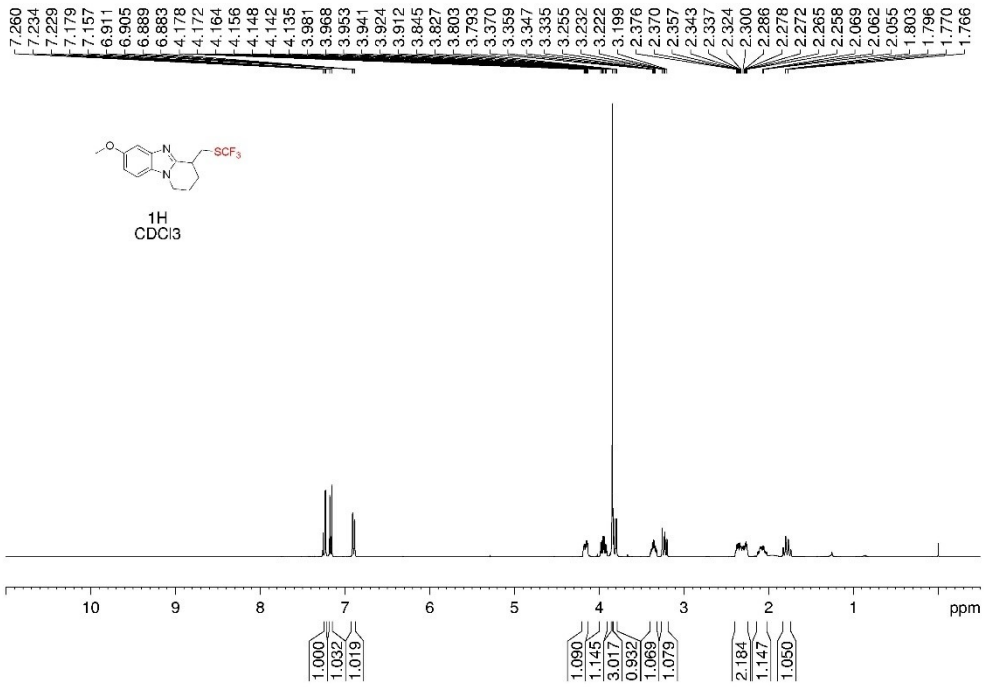



**Figure S18. $^{1}H$ NMR (400 MHz, $CDCl_3$) of compound 3f**

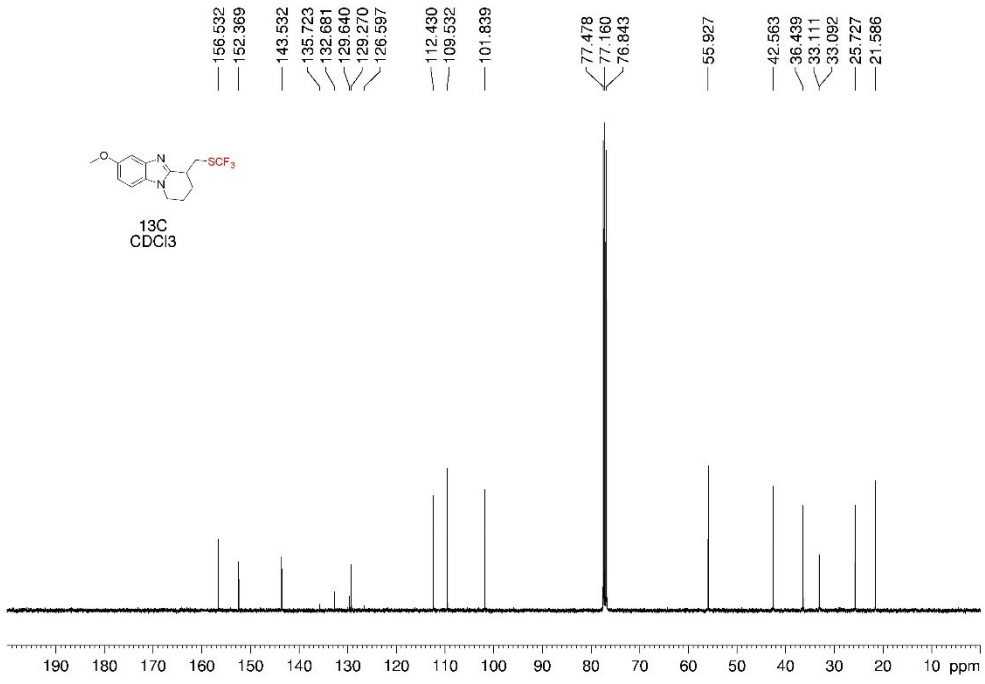



**Figure S19. $^{13}C$ NMR (100 MHz, $CDCl_3$) of compound 3f**

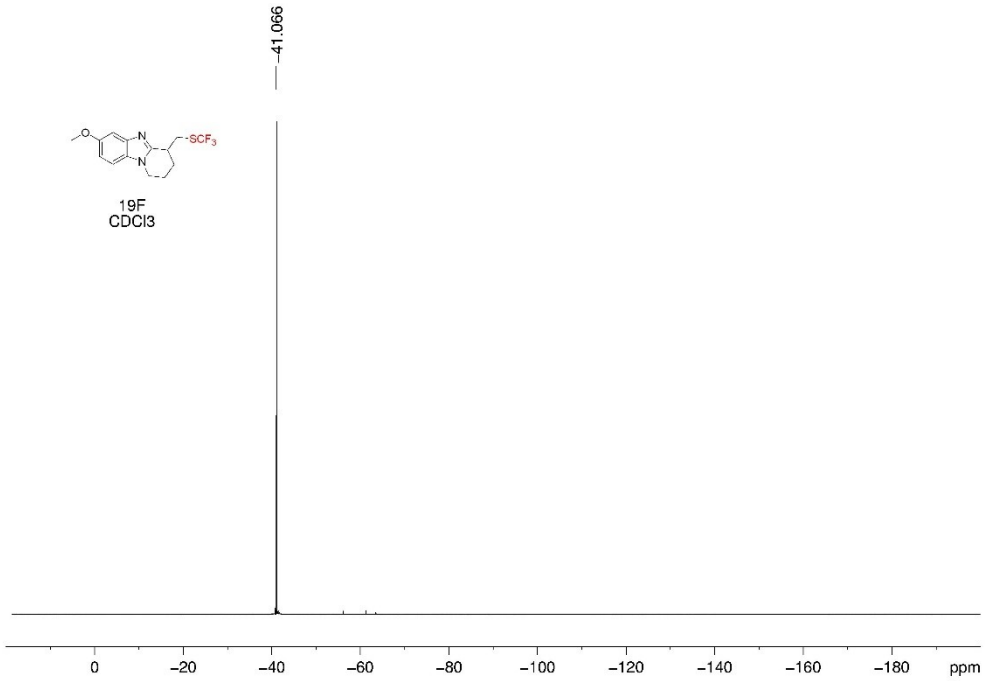



**Figure S20. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3f**

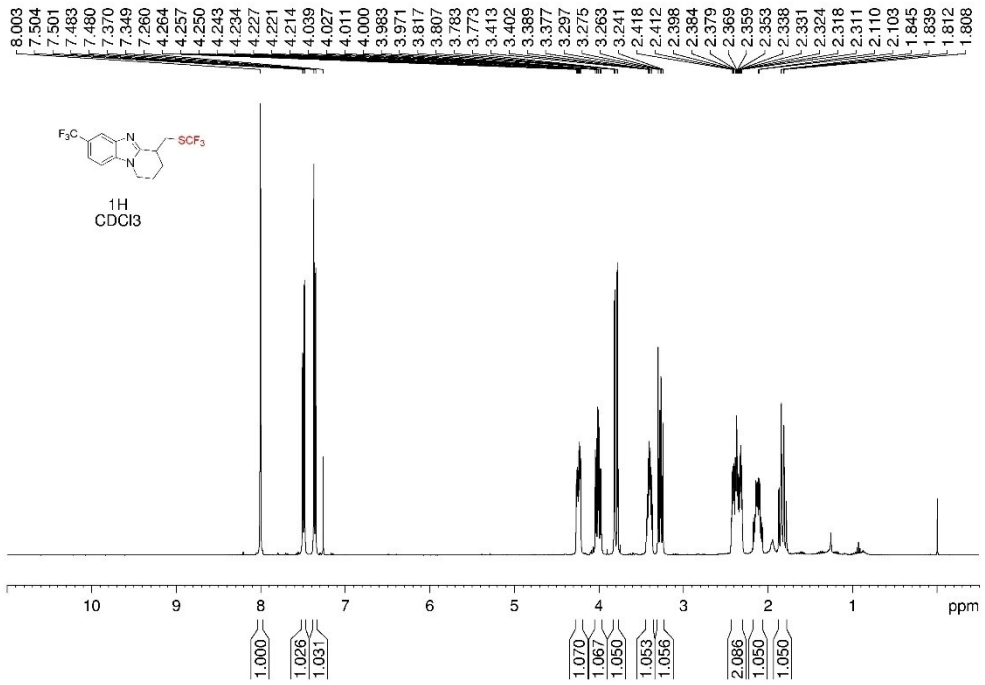



**Figure S21. $^{1}$H NMR (400 MHz, $CDCl_3$) of compound 3g**

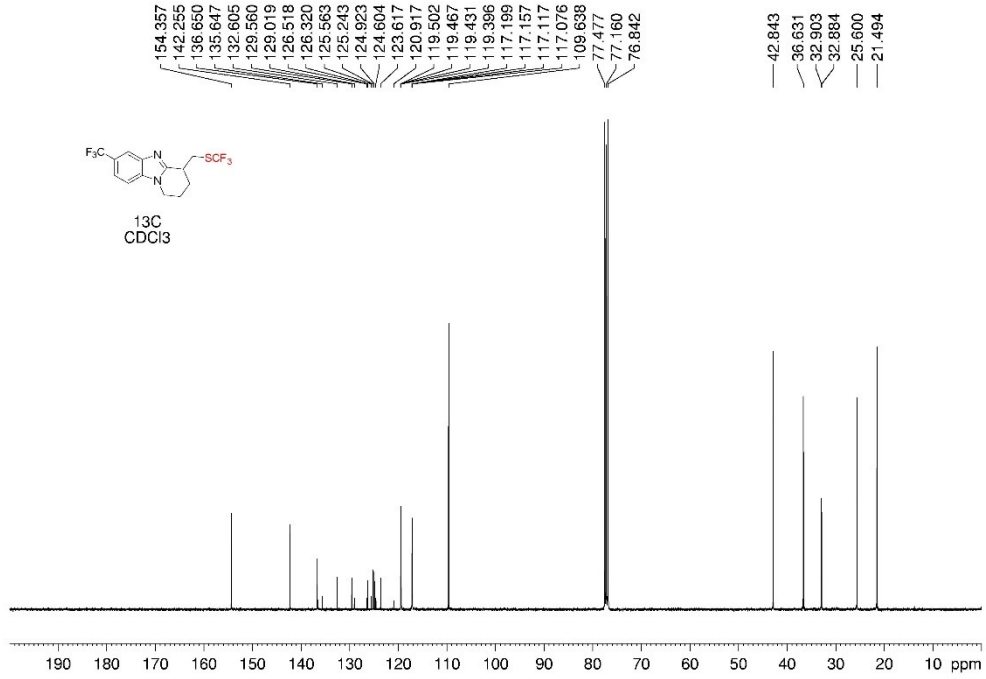



**Figure S22. $^{13}$C NMR (100 MHz, $CDCl_3$) of compound 3g**

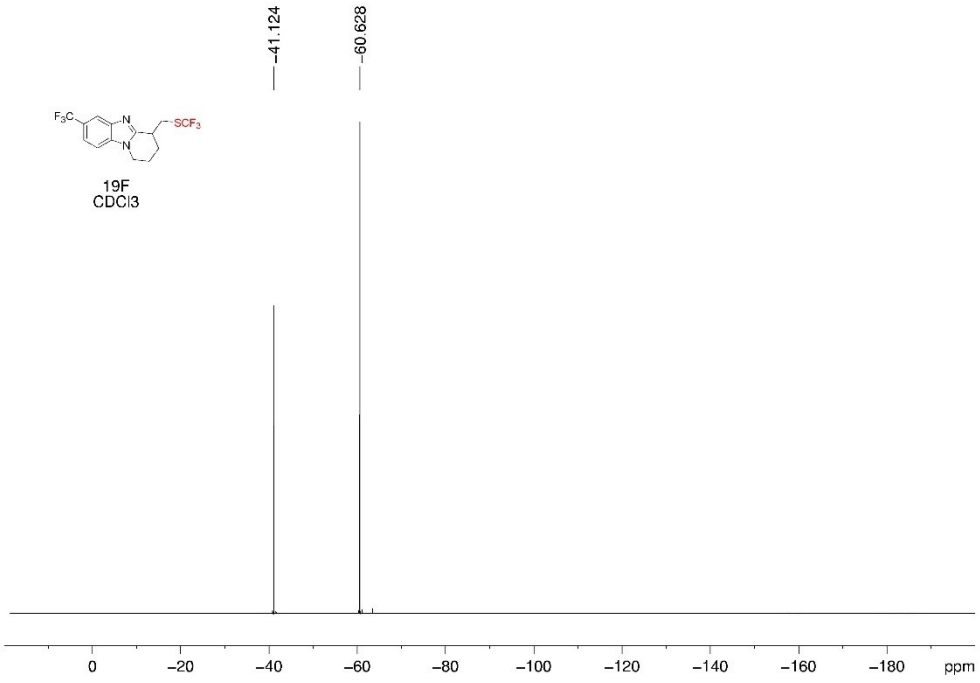



**Figure S23. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3g**

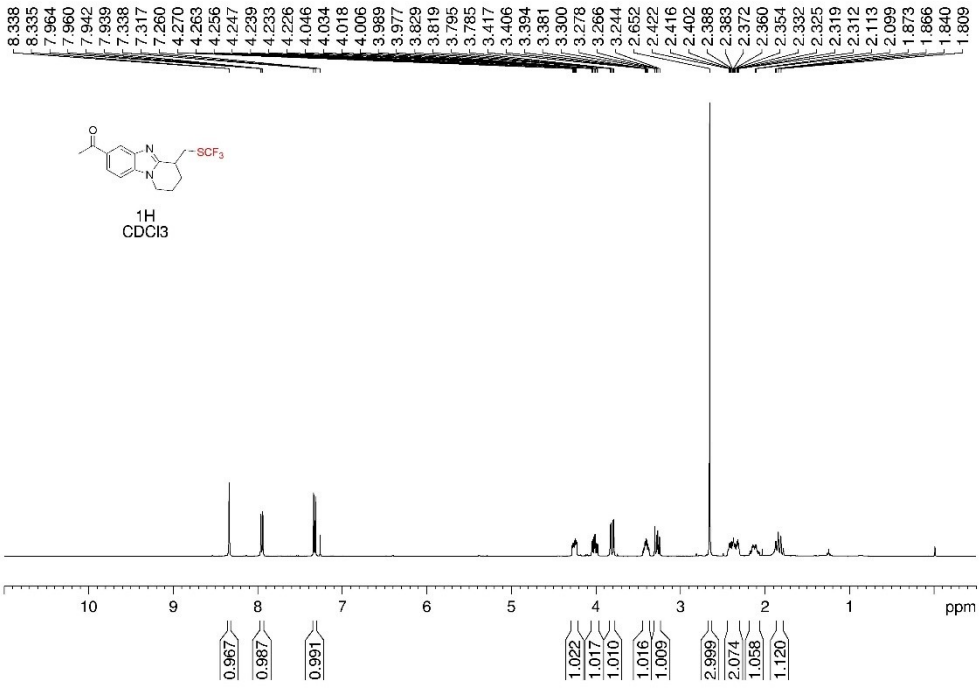



**Figure S24. $^{1}H$ NMR (400 MHz, $CDCl_3$) of compound 3h**

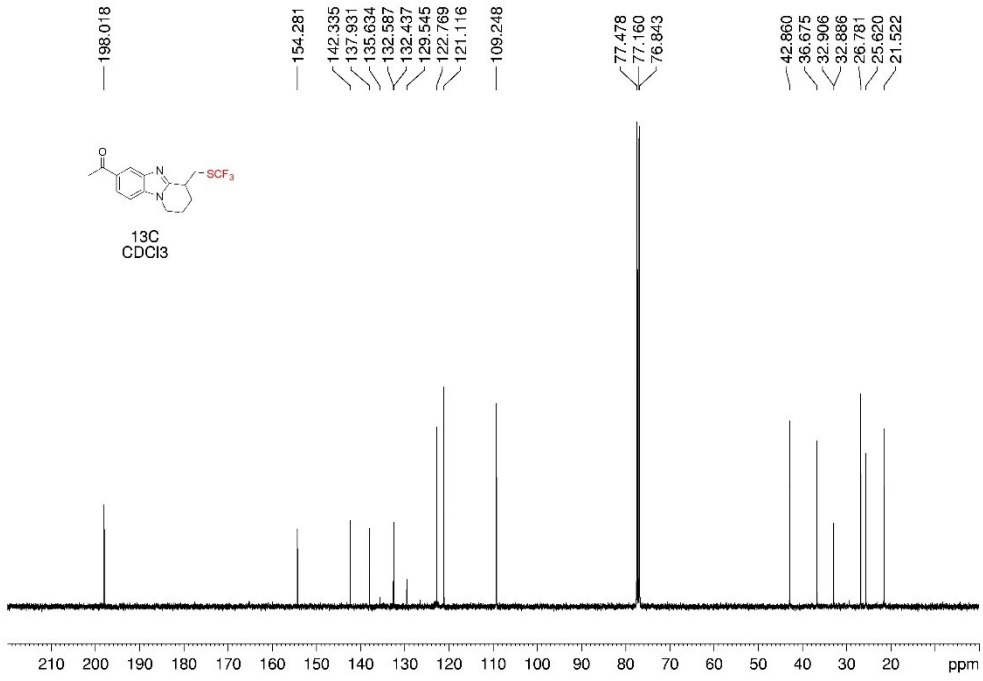



**Figure S25. $^{13}C$ NMR (100 MHz, $CDCl_3$) of compound 3h**

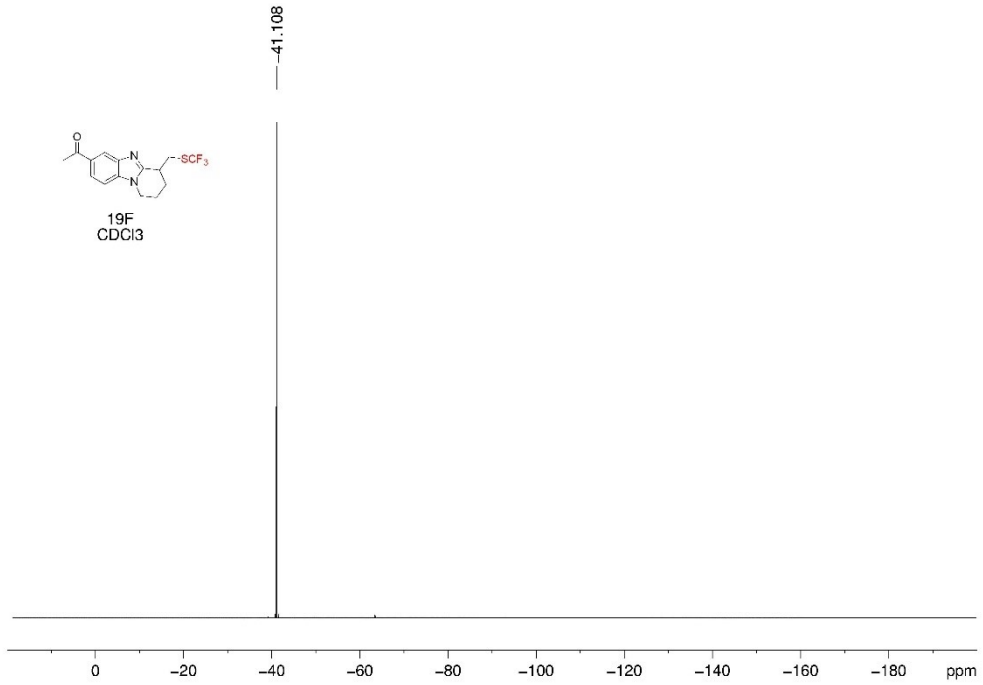



**Figure S26. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3h**

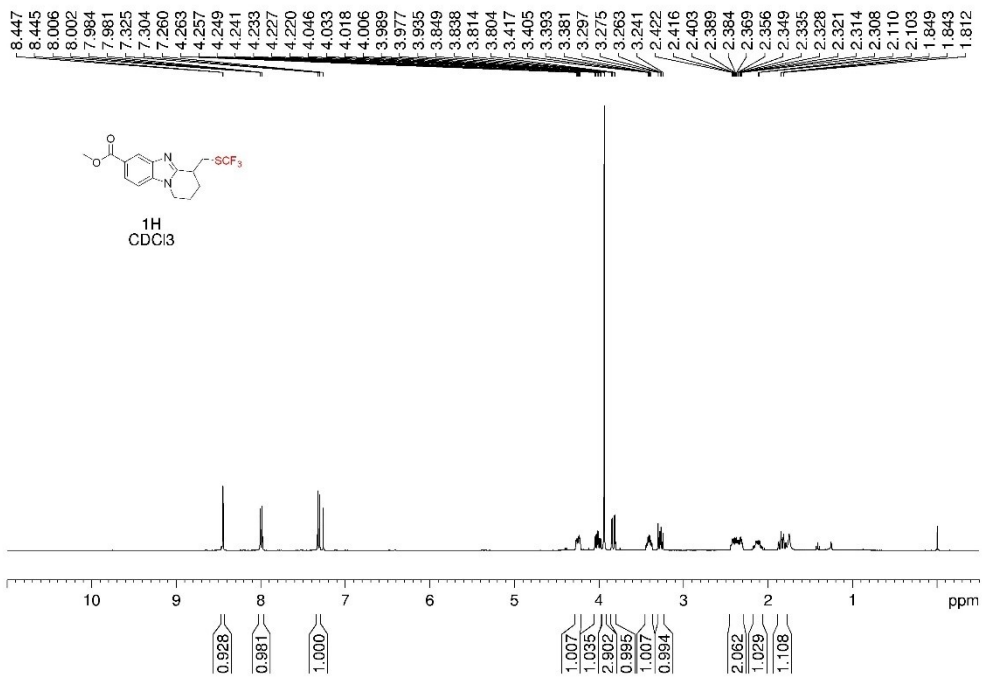



**Figure S27. $^{1}$H NMR (400 MHz, $CDCl_3$) of compound 3i**

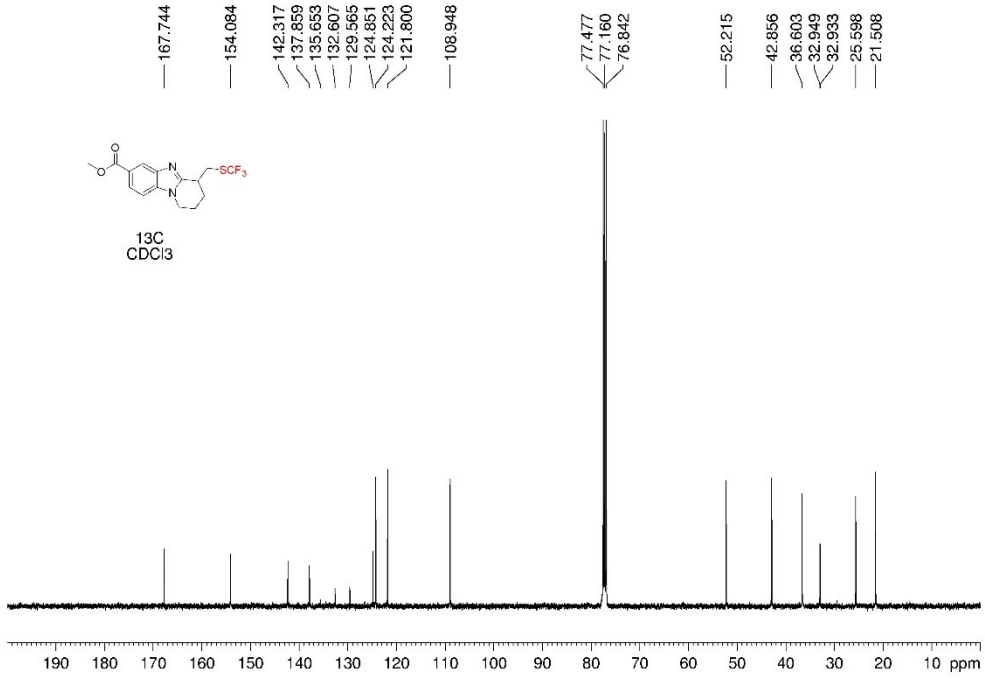



**Figure S28. $^{13}$C NMR (100 MHz, $CDCl_3$) of compound 3i**

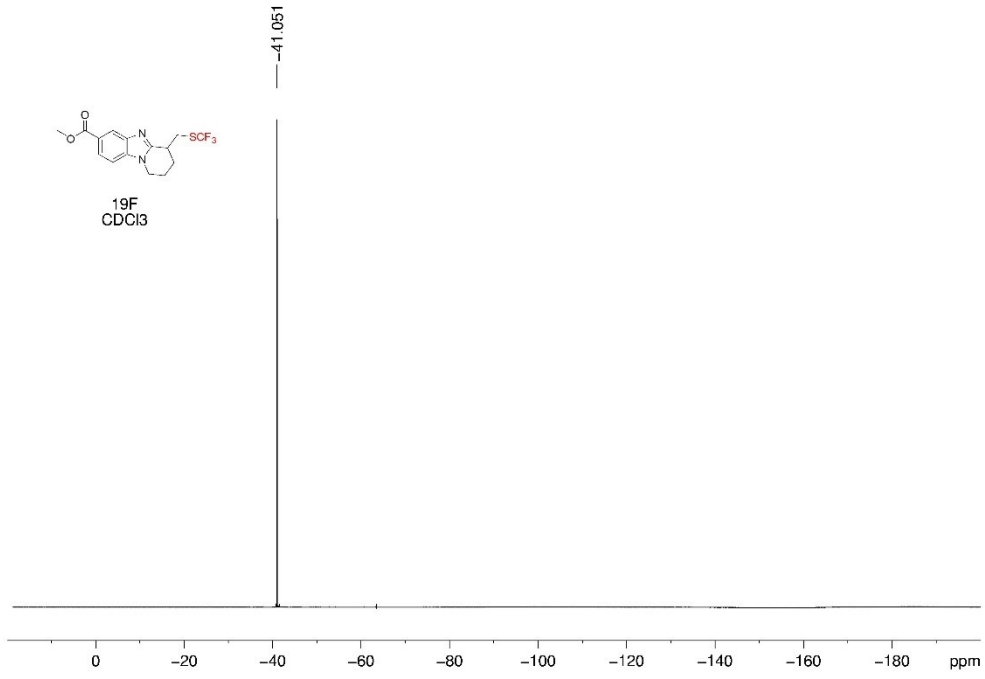



**Figure S29. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3i**

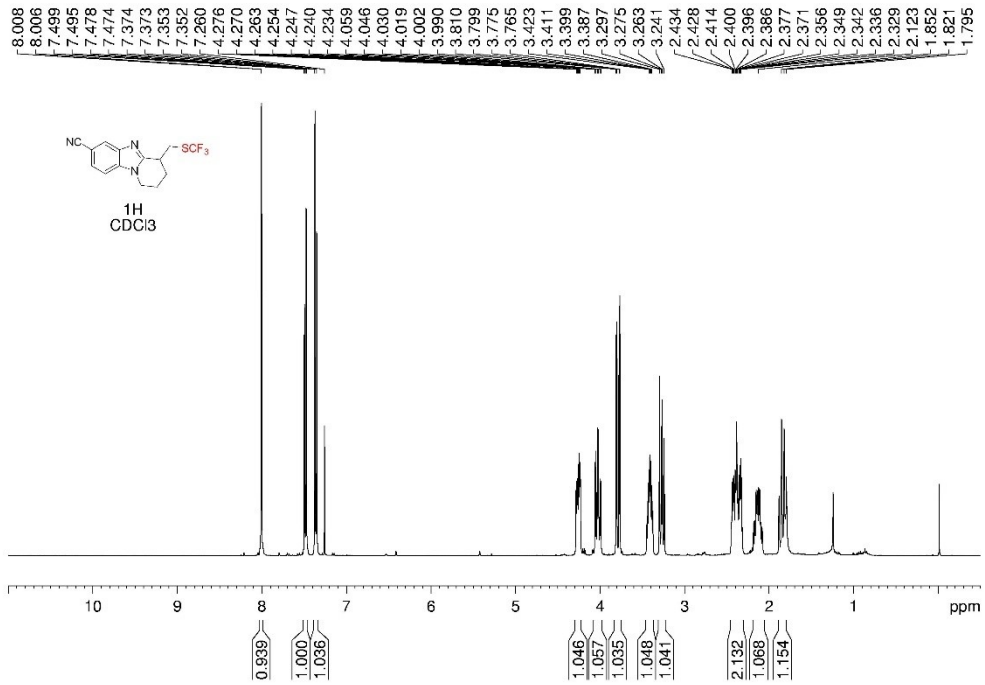



**Figure S30. $^{1}H$ NMR (400 MHz, $CDCl_3$) of compound 3j**

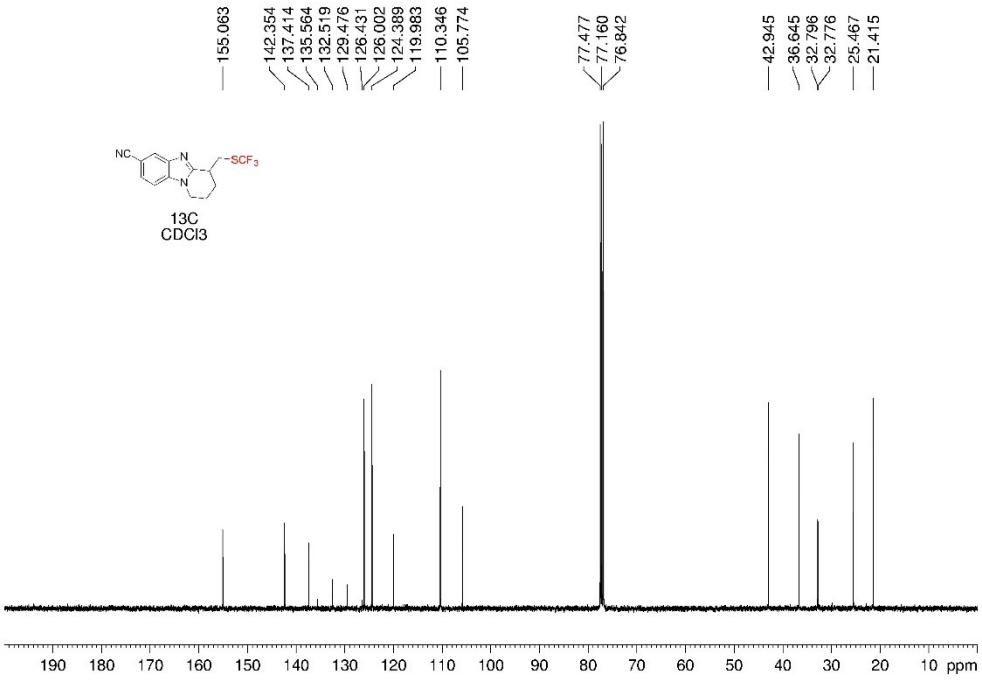



**Figure S31. $^{13}C$ NMR (100 MHz, $CDCl_3$) of compound 3j**

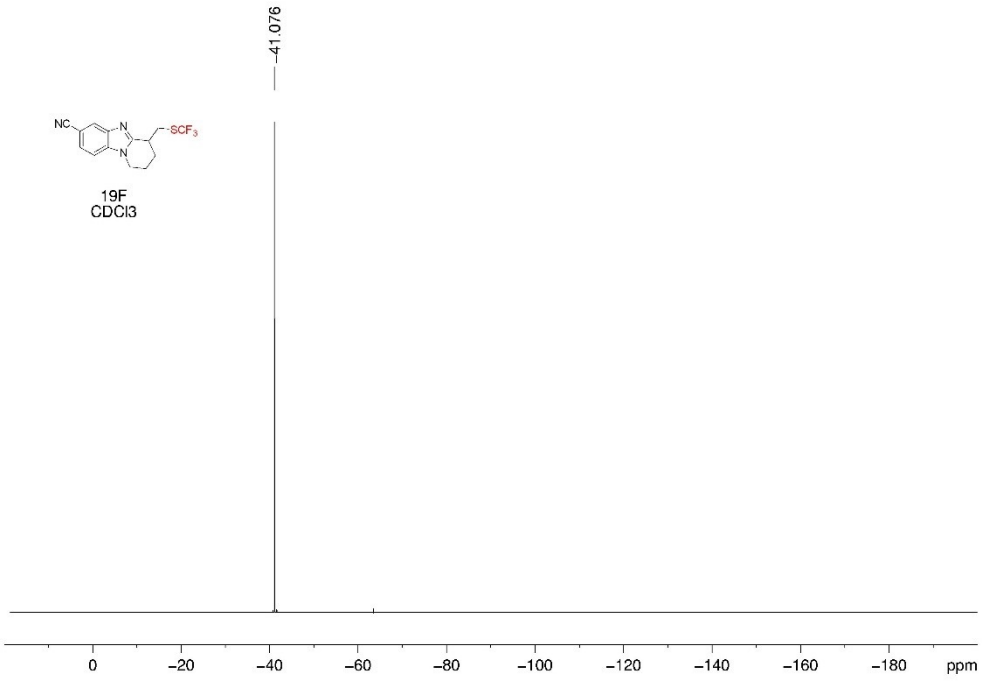



**Figure S32. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3j**

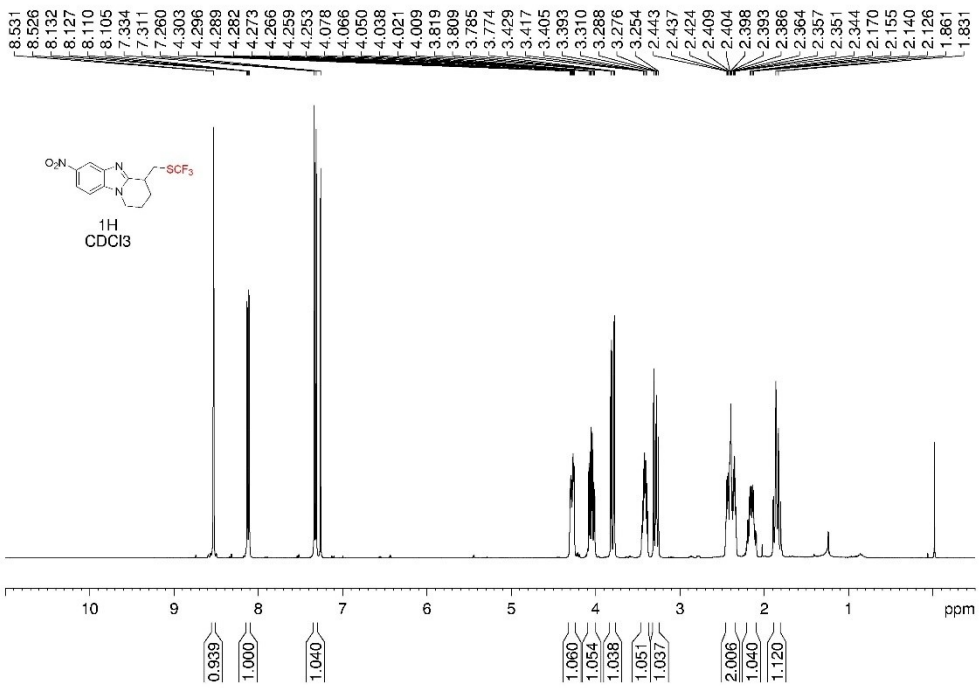



**Figure S33. $^{1}$H NMR (400 MHz, $CDCl_3$) of compound 3k**

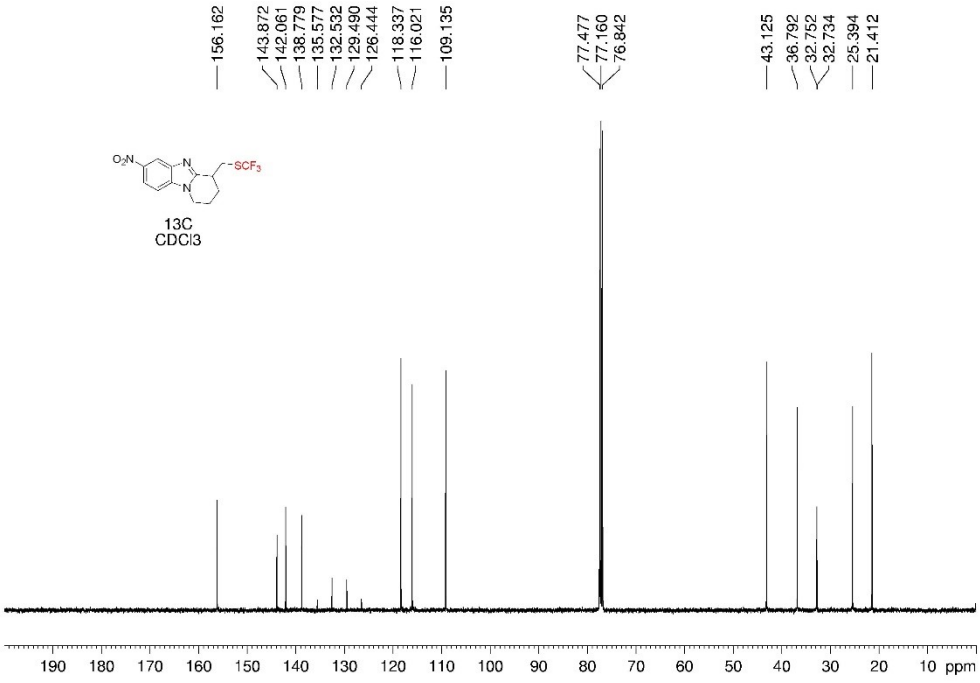



**Figure S34. $^{13}$C NMR (100 MHz, $CDCl_3$) of compound 3k**

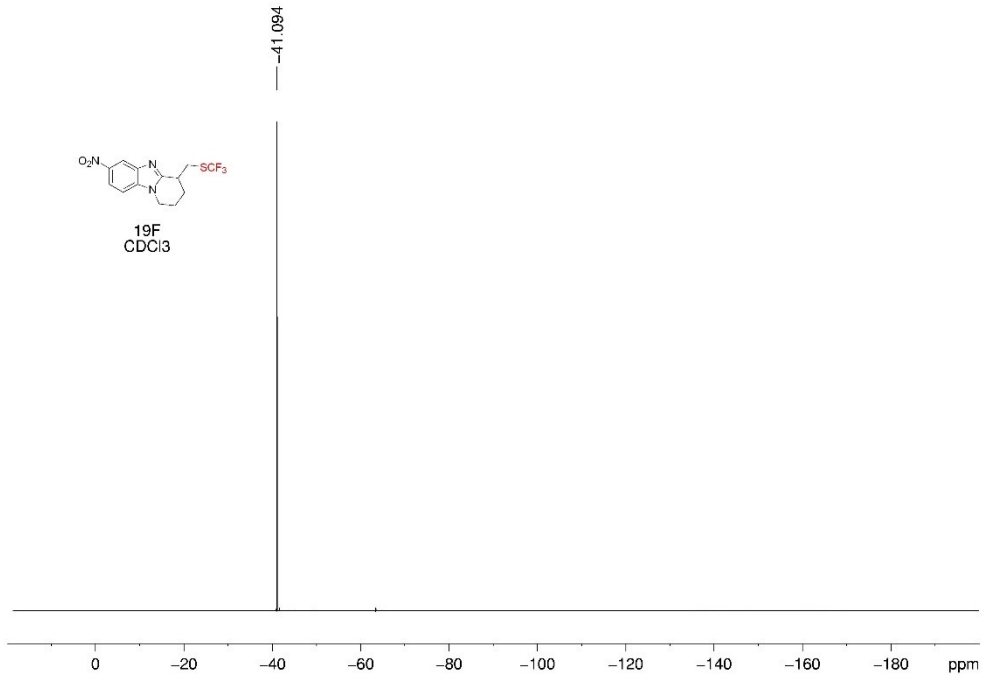



**Figure S35. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3k**

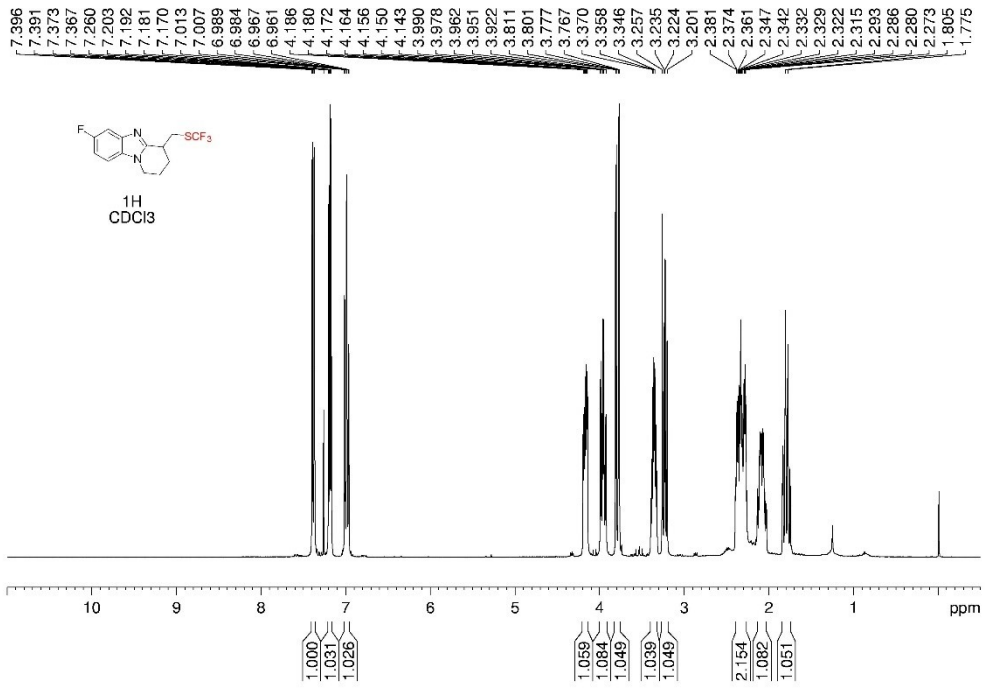



**Figure S36. $^{1}H$ NMR (400 MHz, $CDCl_3$) of compound 3m**

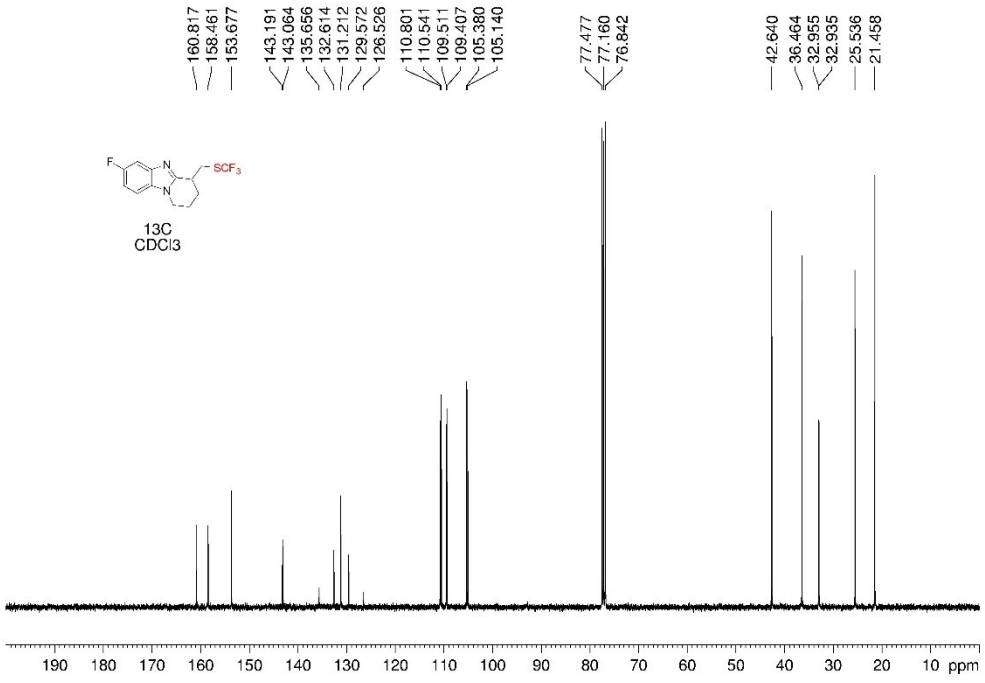



**Figure S37. $^{13}C$ NMR (100 MHz, $CDCl_3$) of compound 3m**

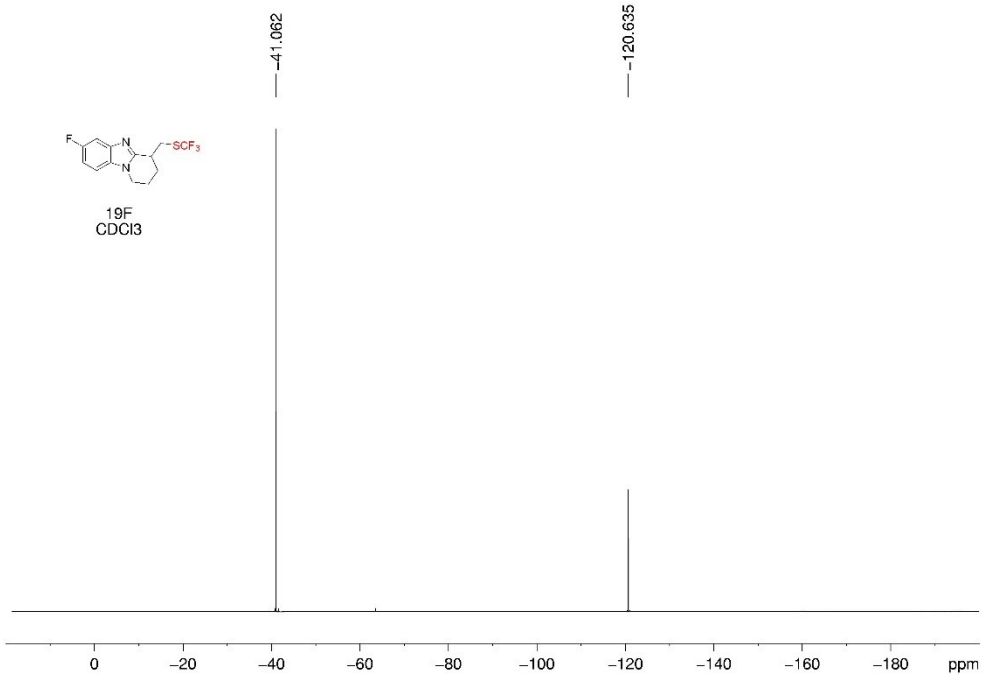



**Figure S38. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3m**

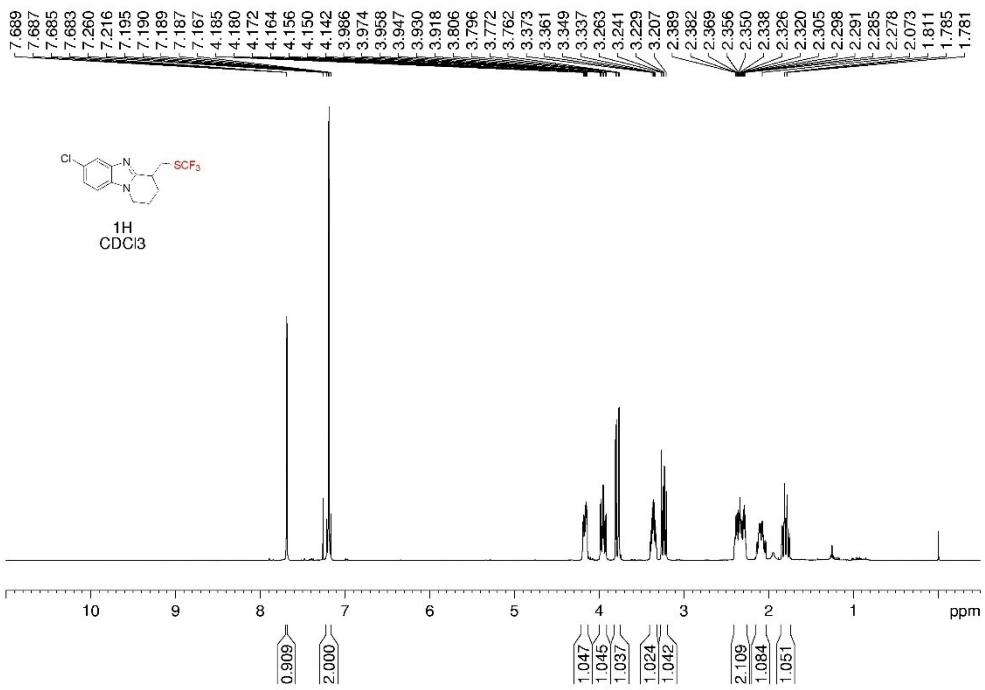



**Figure S39. $^{1}$H NMR (400 MHz, $CDCl_3$) of compound 3n**

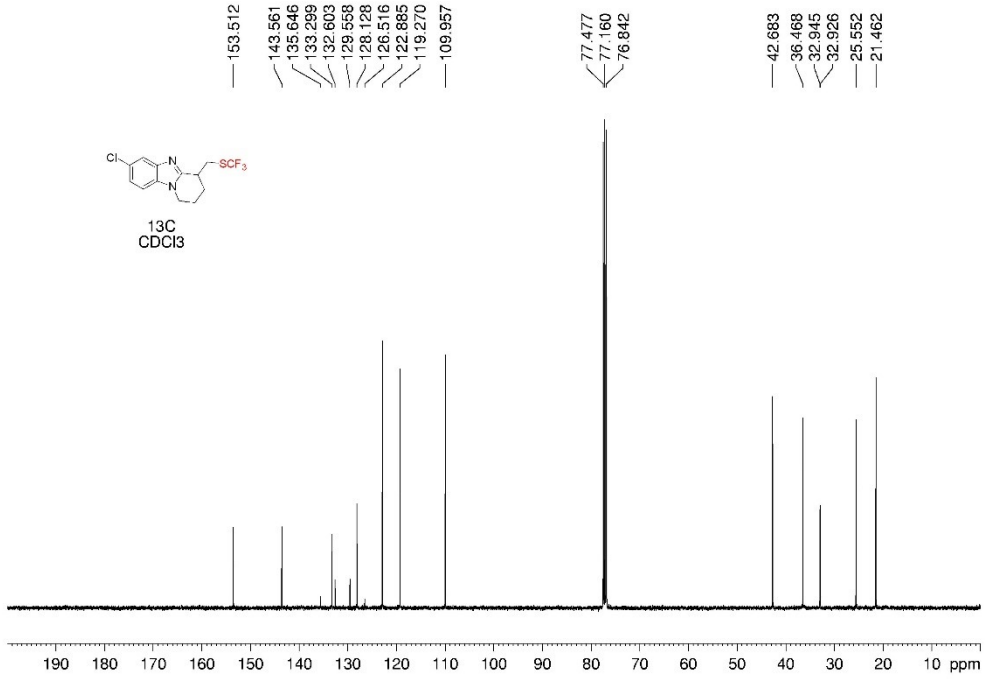



**Figure S40. $^{13}$C NMR (100 MHz, $CDCl_3$) of compound 3n**

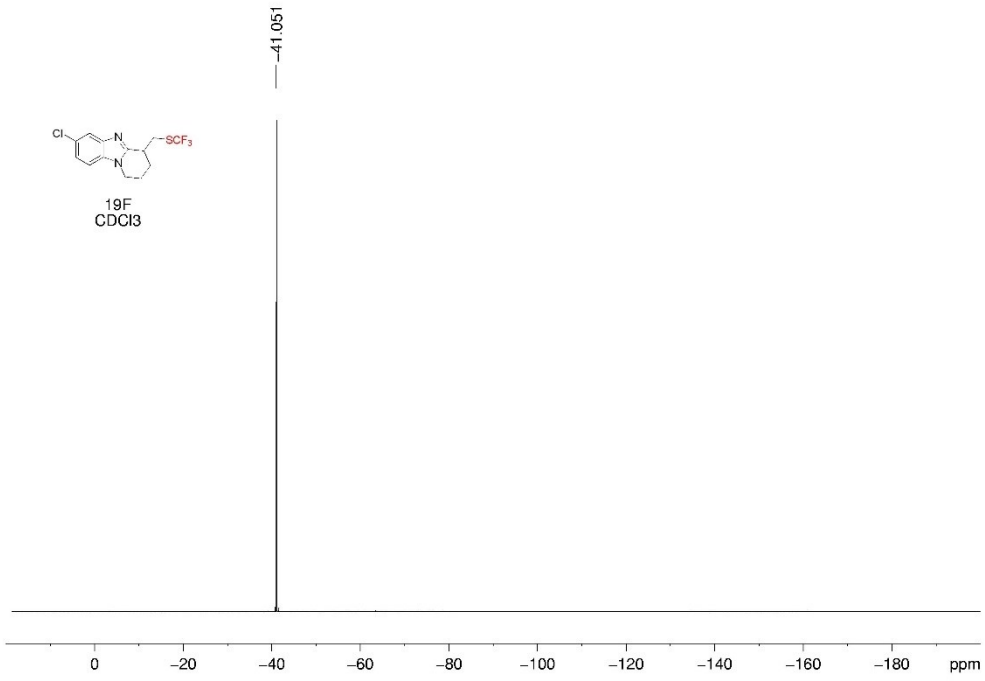



**Figure S41. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3n**

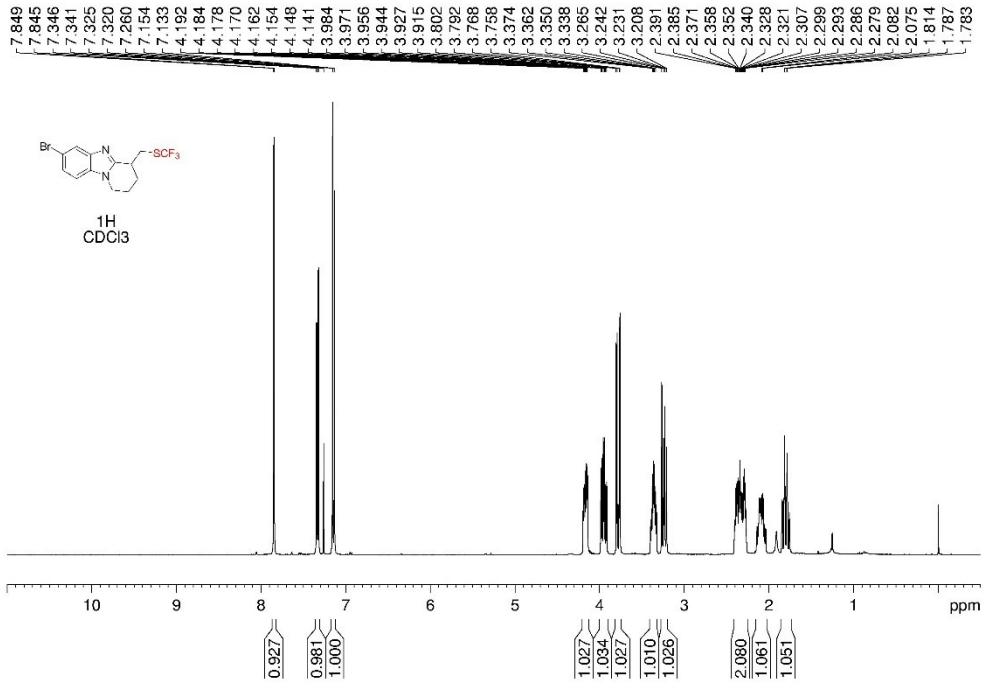



**Figure S42. $^{1}H$ NMR (400 MHz, $CDCl_3$) of compound 3o**

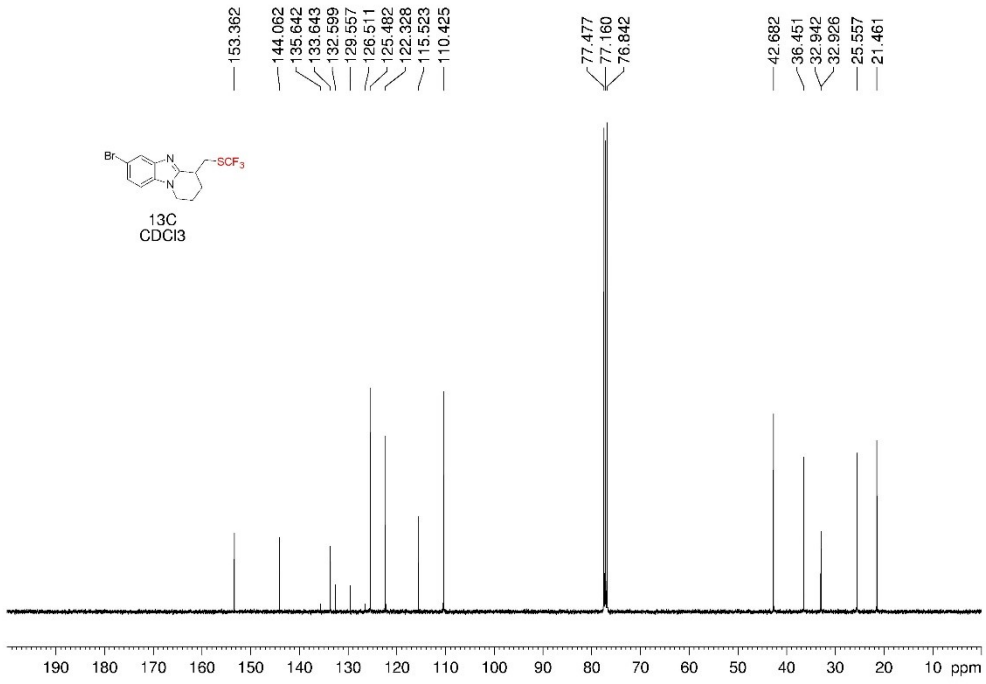



**Figure S43. $^{13}C$ NMR (100 MHz, $CDCl_3$) of compound 3o**

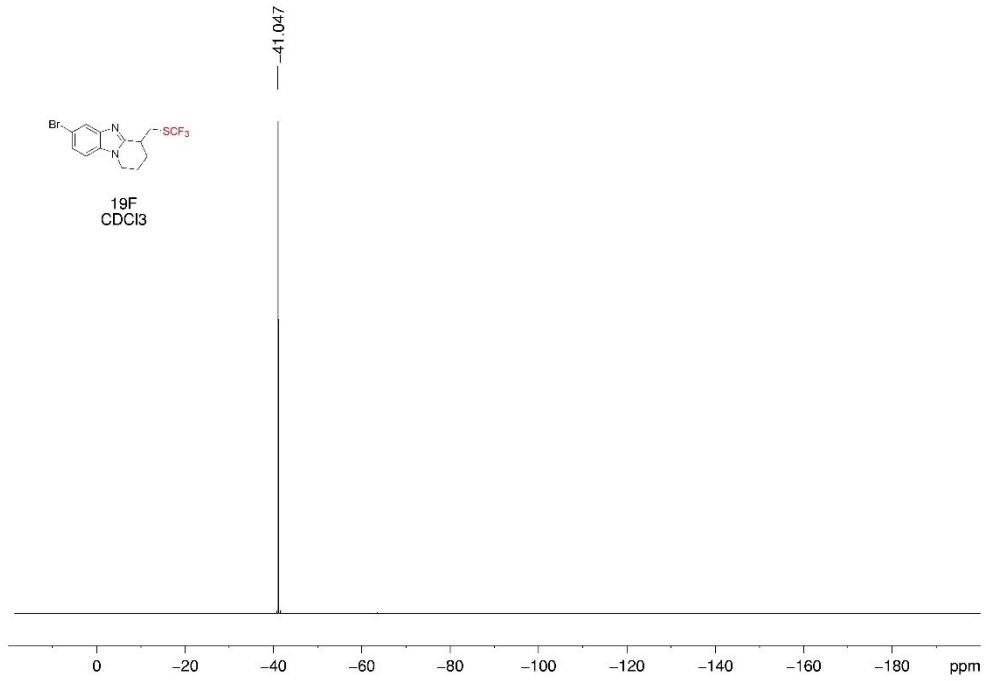



**Figure S44. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3o**

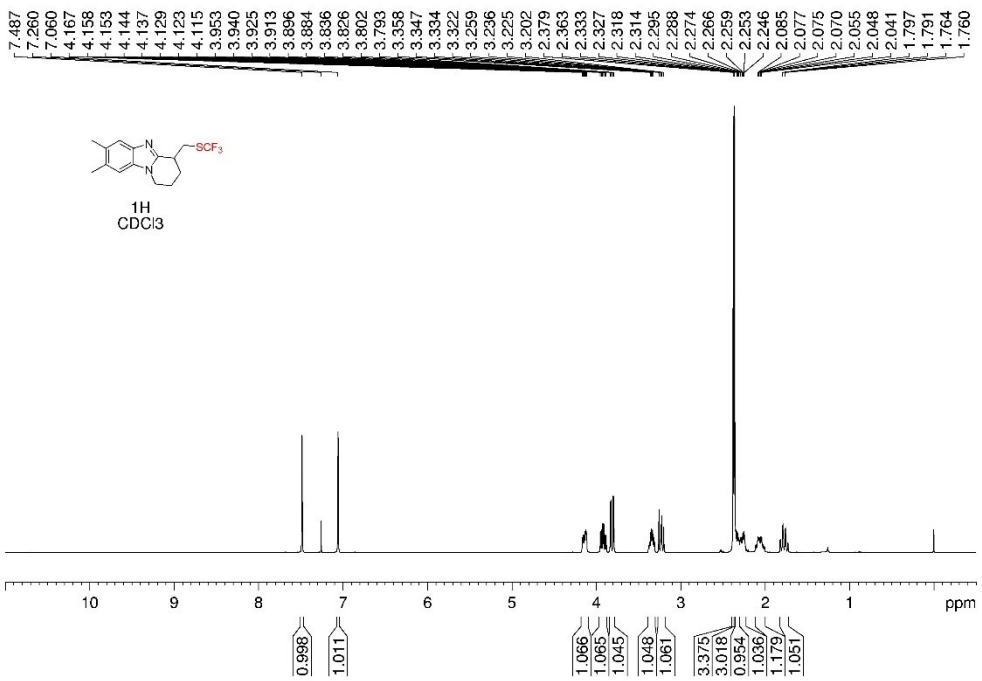



**Figure S45. $^{1}$H NMR (400 MHz, $CDCl_3$) of compound 3p**

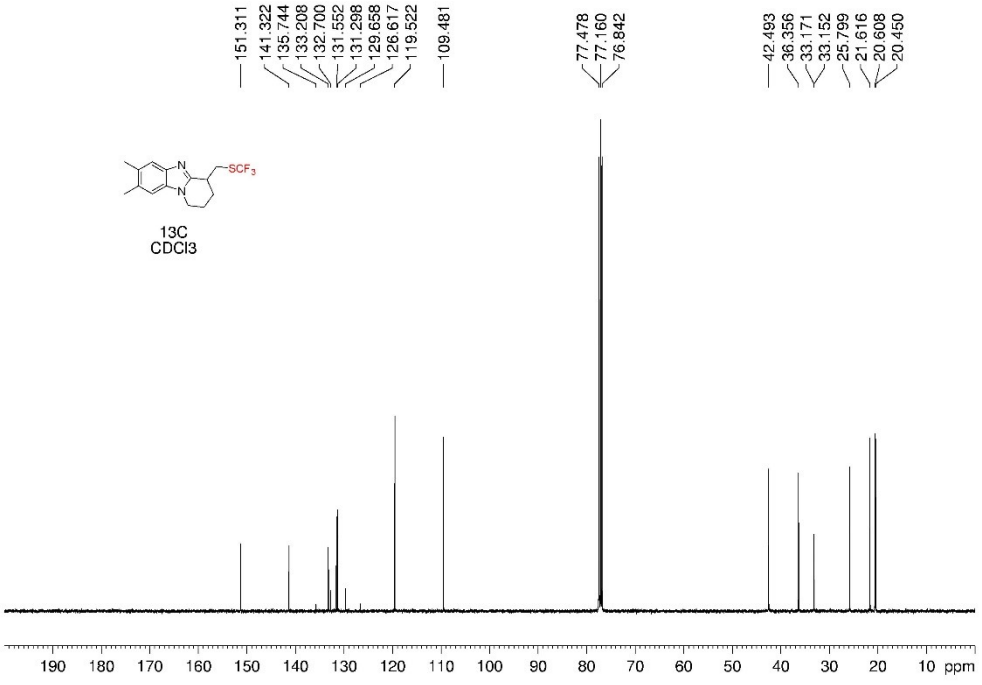



**Figure S46. $^{13}$C NMR (100 MHz, $CDCl_3$) of compound 3p**

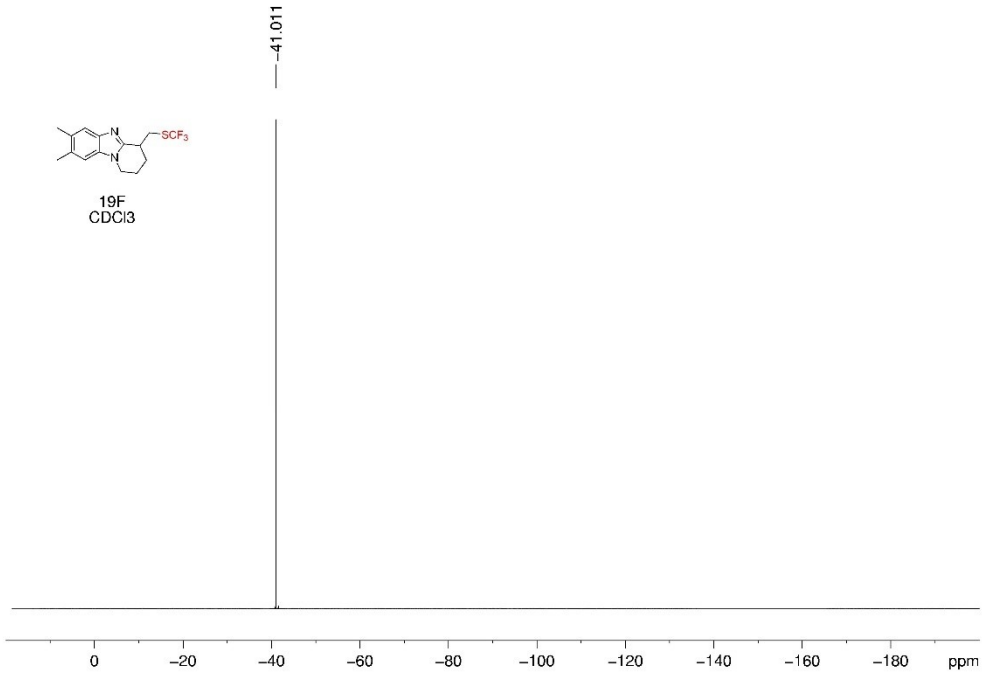



**Figure S47. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3p**

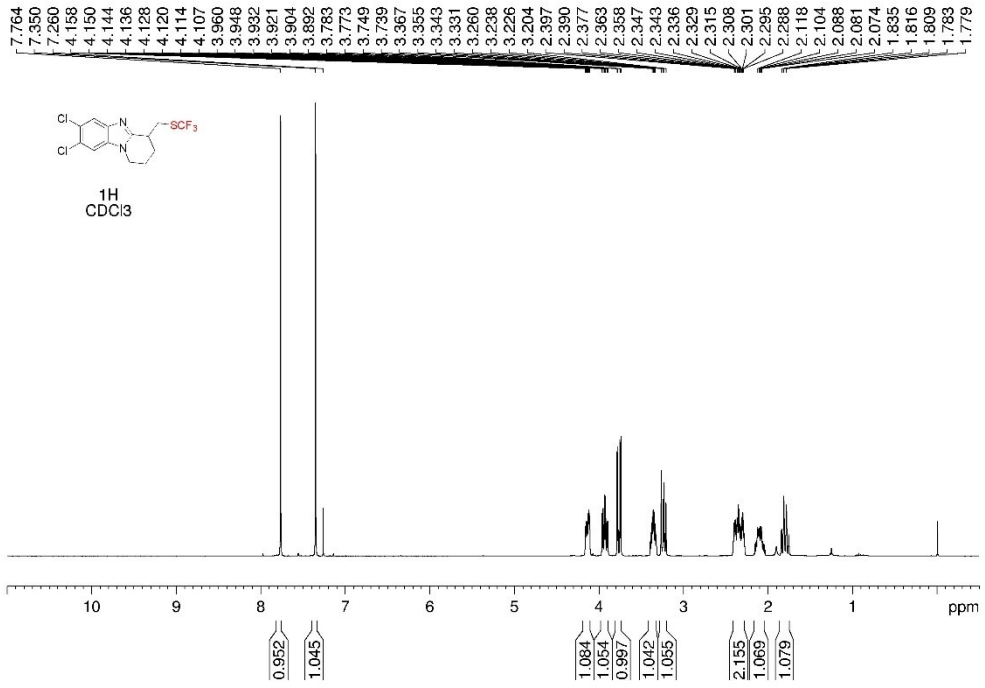



**Figure S48. $^{1}H$ NMR (400 MHz, $CDCl_3$) of compound 3q**

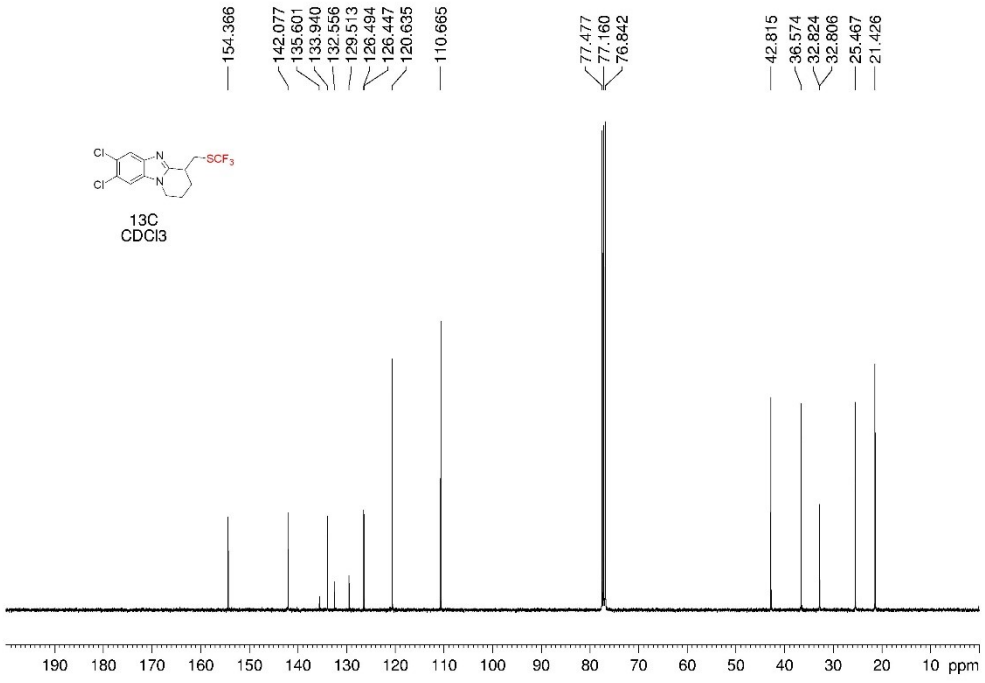



**Figure S49. $^{13}C$ NMR (100 MHz, $CDCl_3$) of compound 3q**

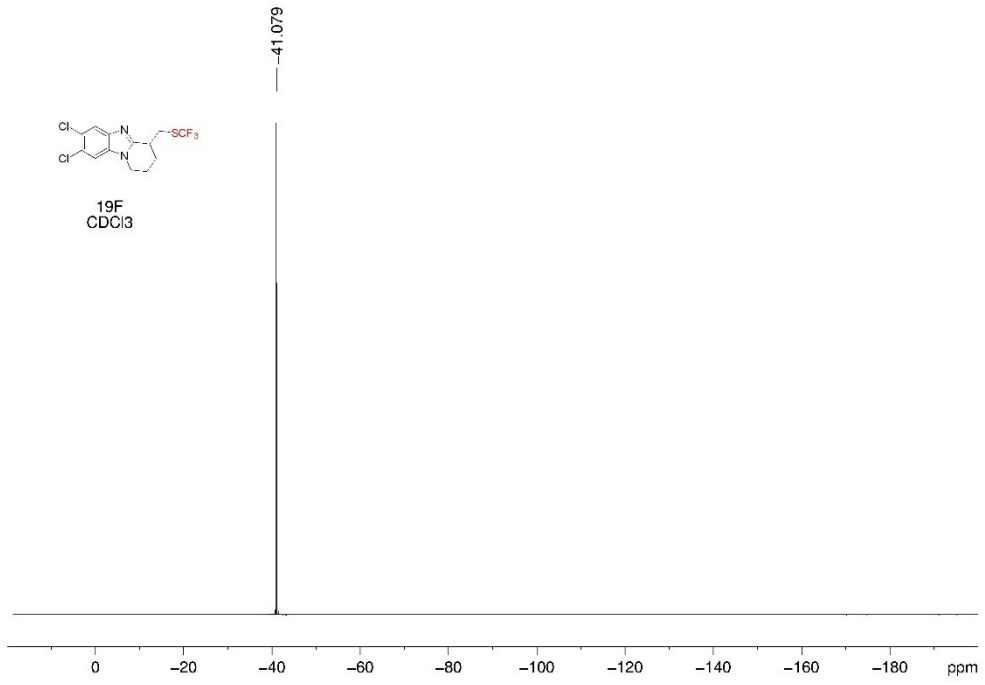



**Figure S50. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3q**

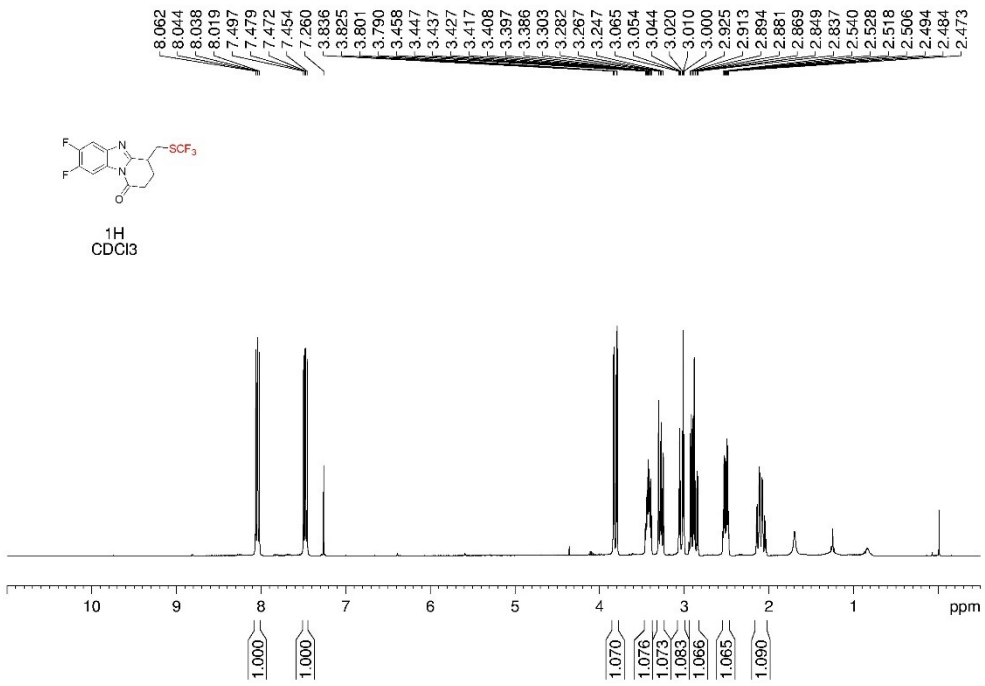



**Figure S51. $^{1}$H NMR (400 MHz, $CDCl_3$) of compound 3s**

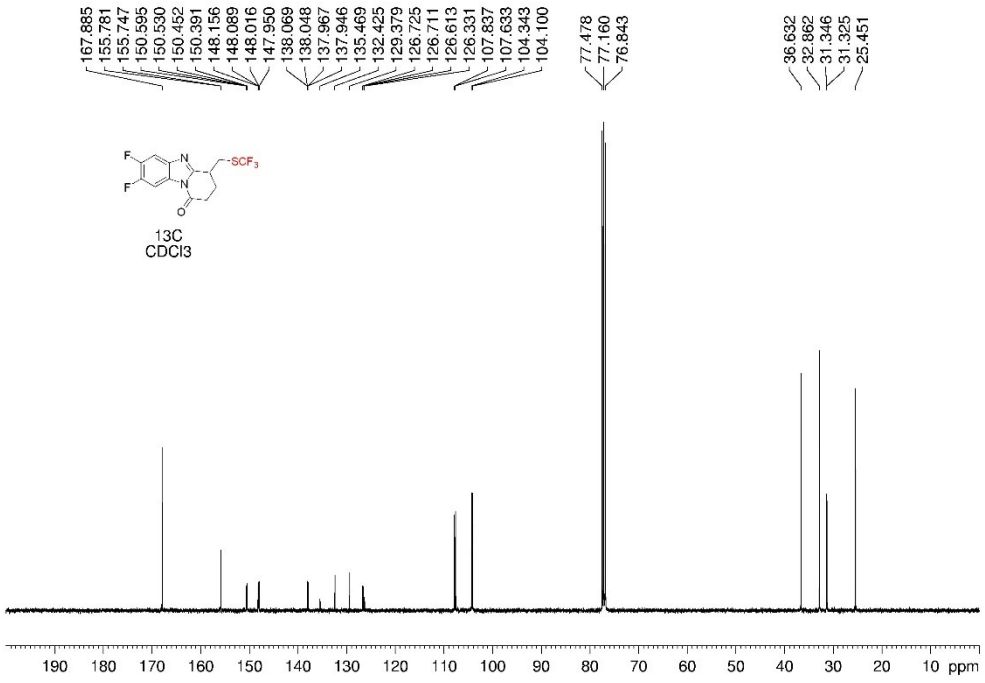



**Figure S52. $^{13}$C NMR (100 MHz, $CDCl_3$) of compound 3s**

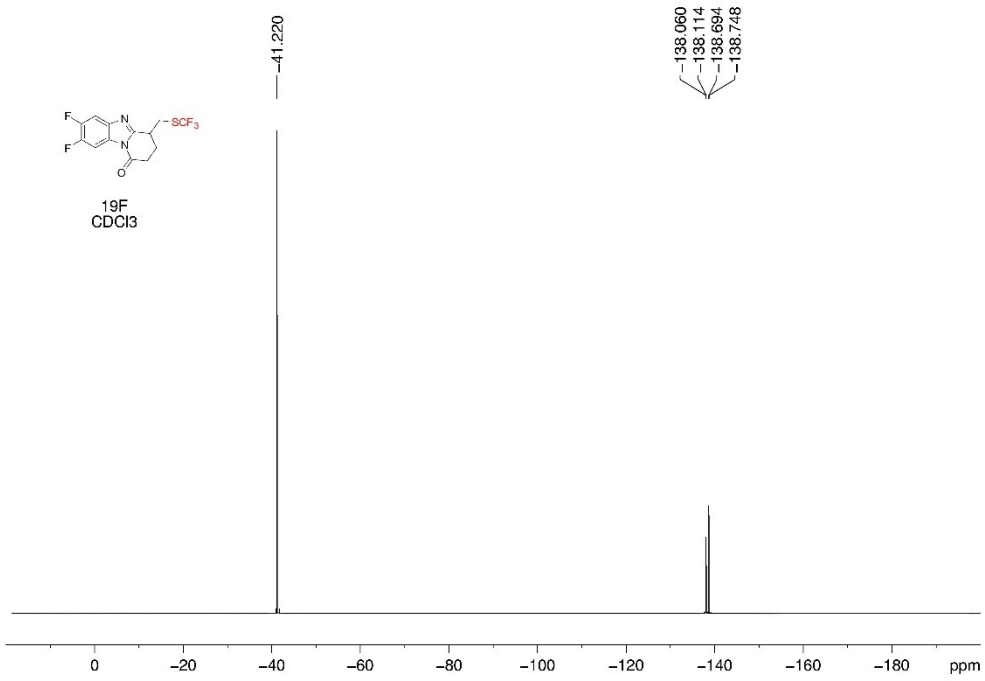



**Figure S53. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3s**

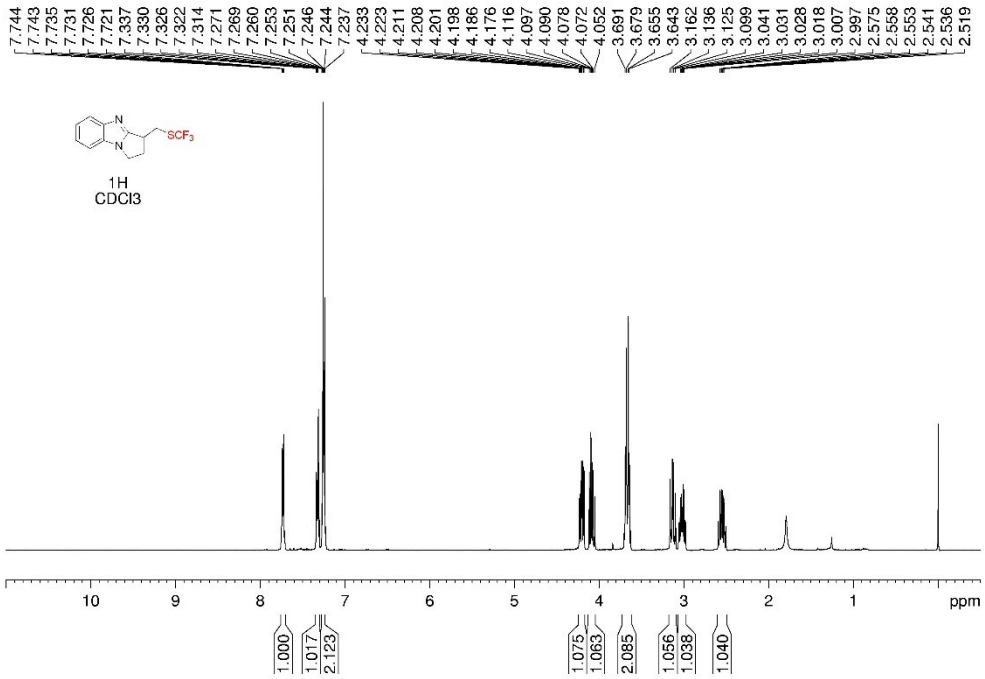



**Figure S54. $^{1}H$ NMR (400 MHz, $CDCl_3$) of compound 3t**

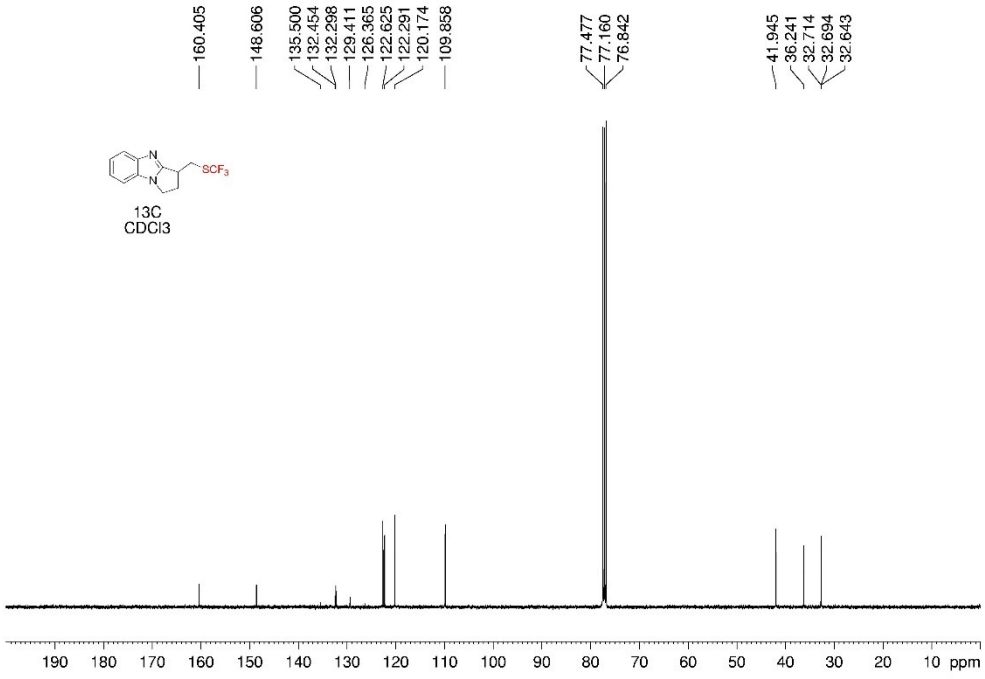



**Figure S55. $^{13}C$ NMR (100 MHz, $CDCl_3$) of compound 3t**

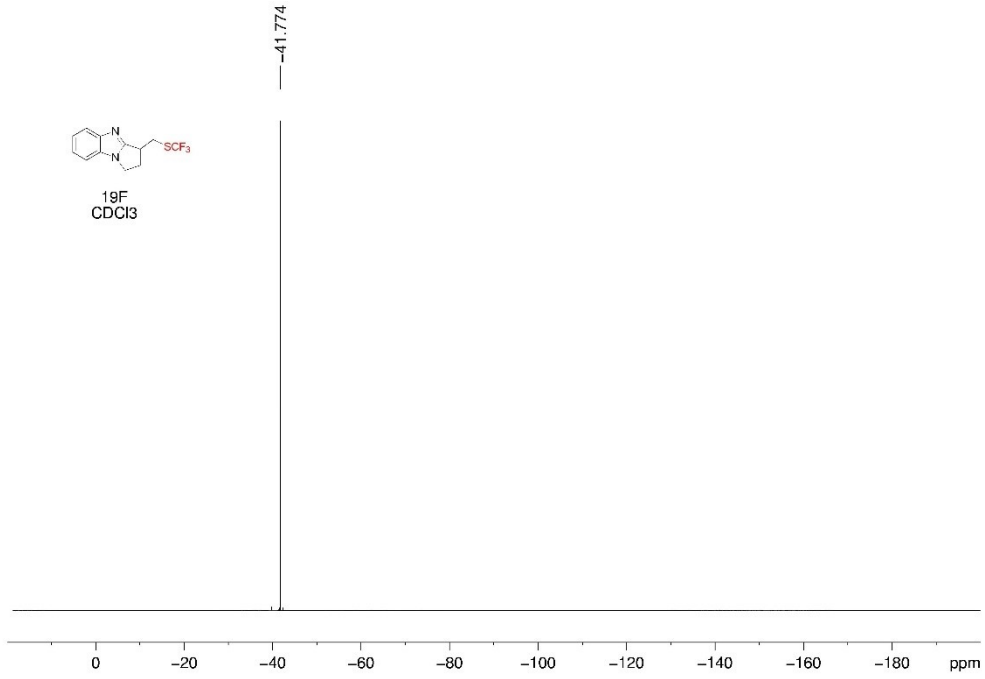



**Figure S56. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3t**

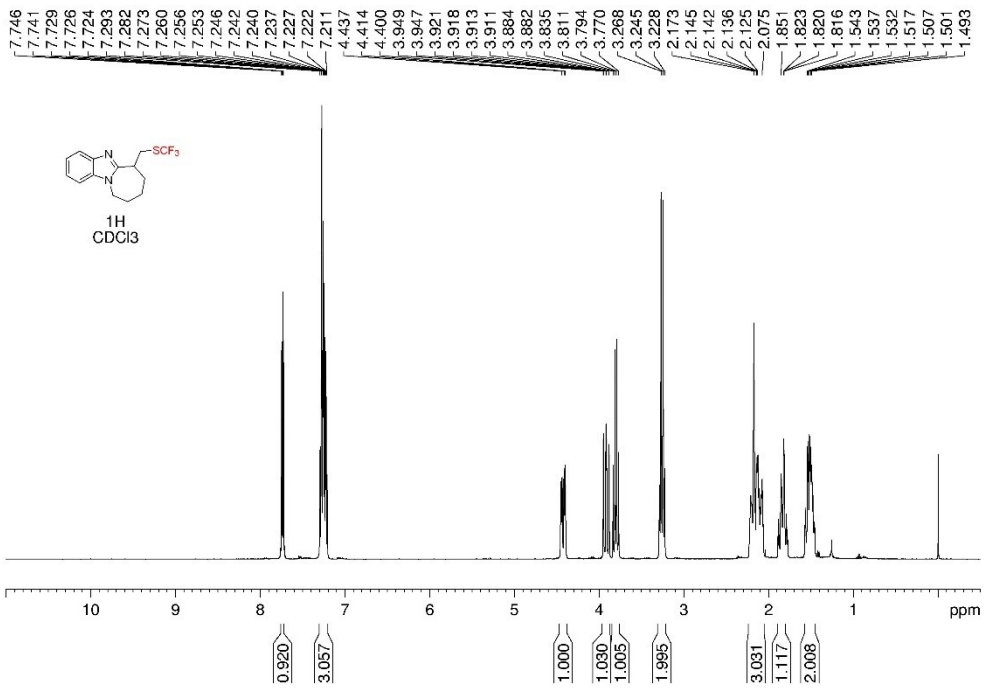



**Figure S57. $^{1}$H NMR (400 MHz, $CDCl_3$) of compound 3u**

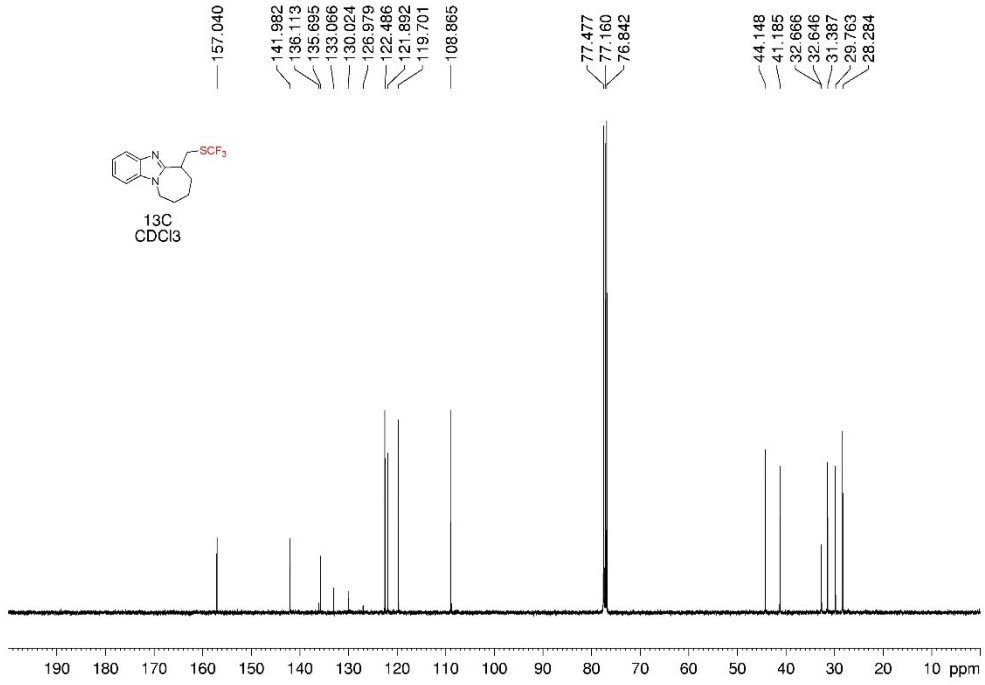



**Figure S58. $^{13}$C NMR (100 MHz, $CDCl_3$) of compound 3u**

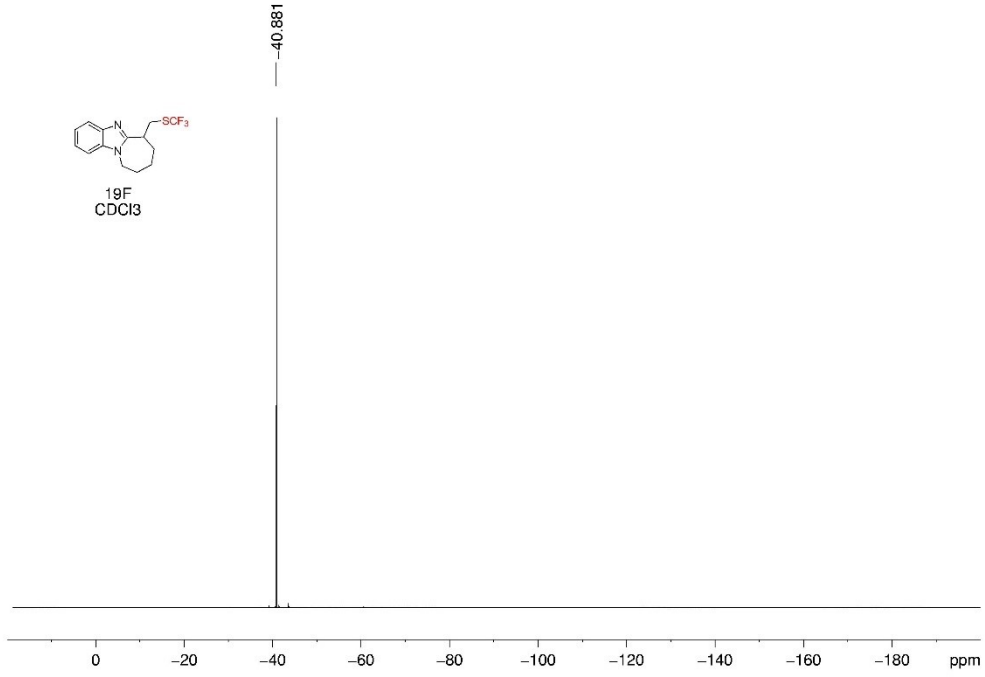



**Figure S59. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3u**

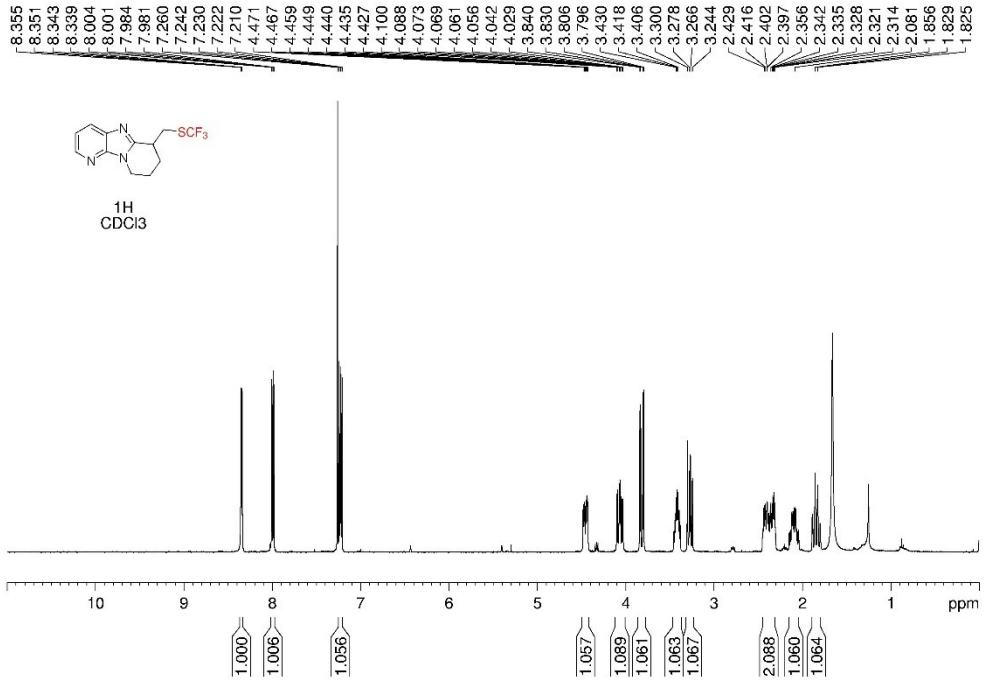



**Figure S60. $^{1}H$ NMR (400 MHz, $CDCl_3$) of compound 3w**

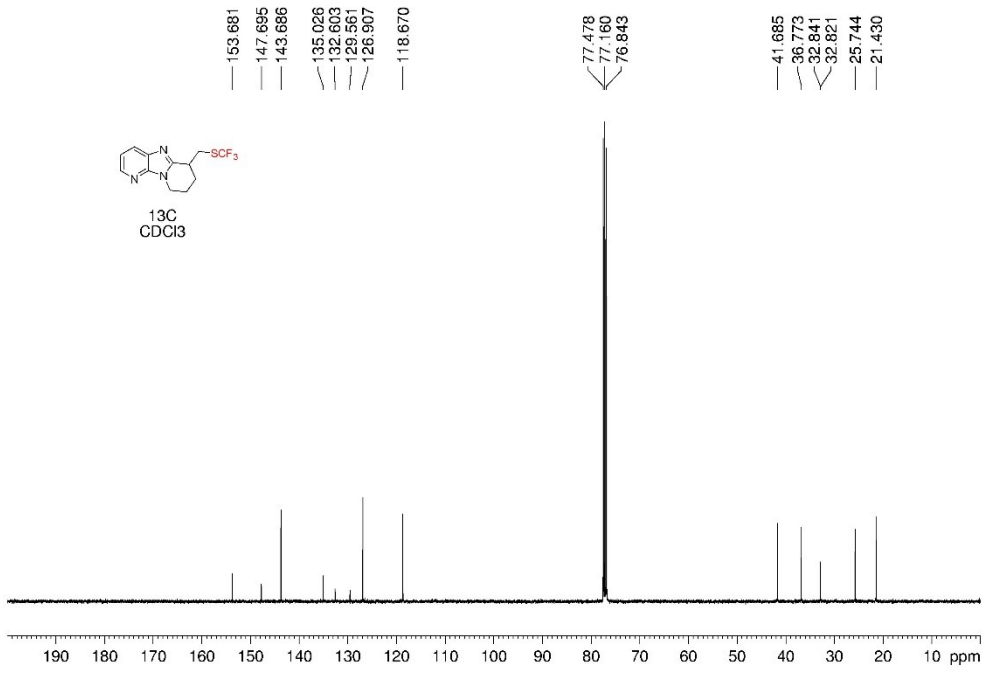



**Figure S61. $^{13}C$ NMR (100 MHz, $CDCl_3$) of compound 3w**

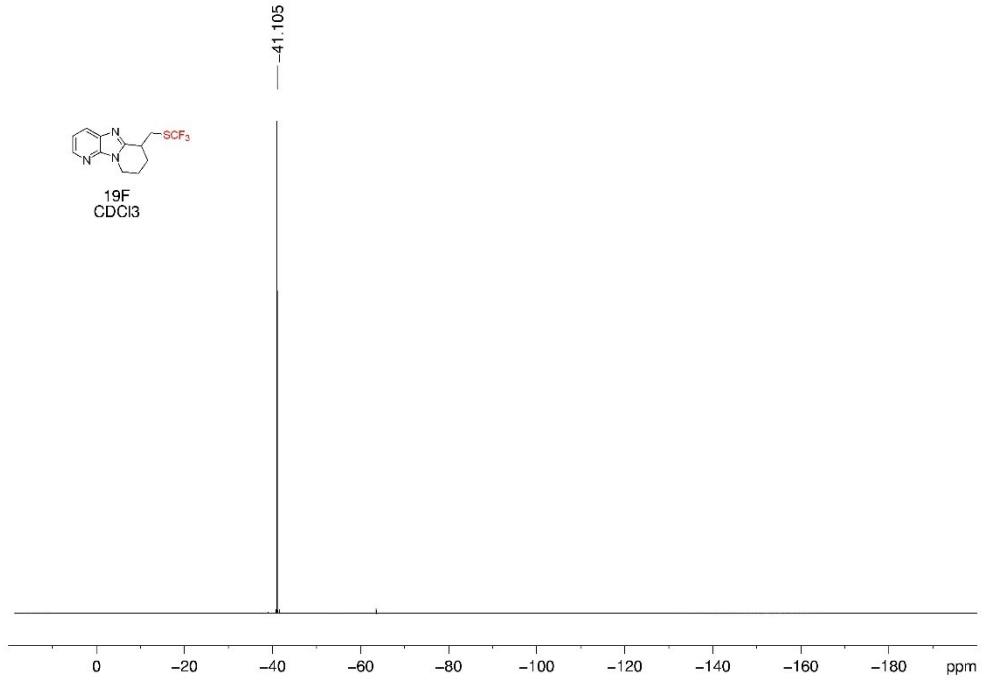



**Figure S62. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3w**

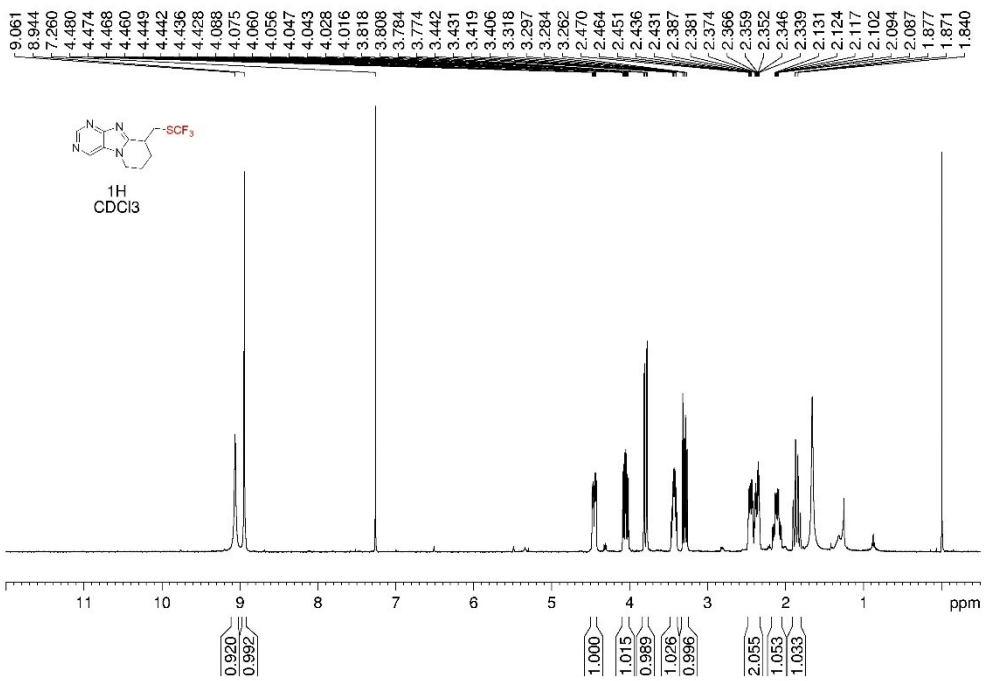



**Figure S63. $^{1}$H NMR (400 MHz, $CDCl_3$) of compound 3y**

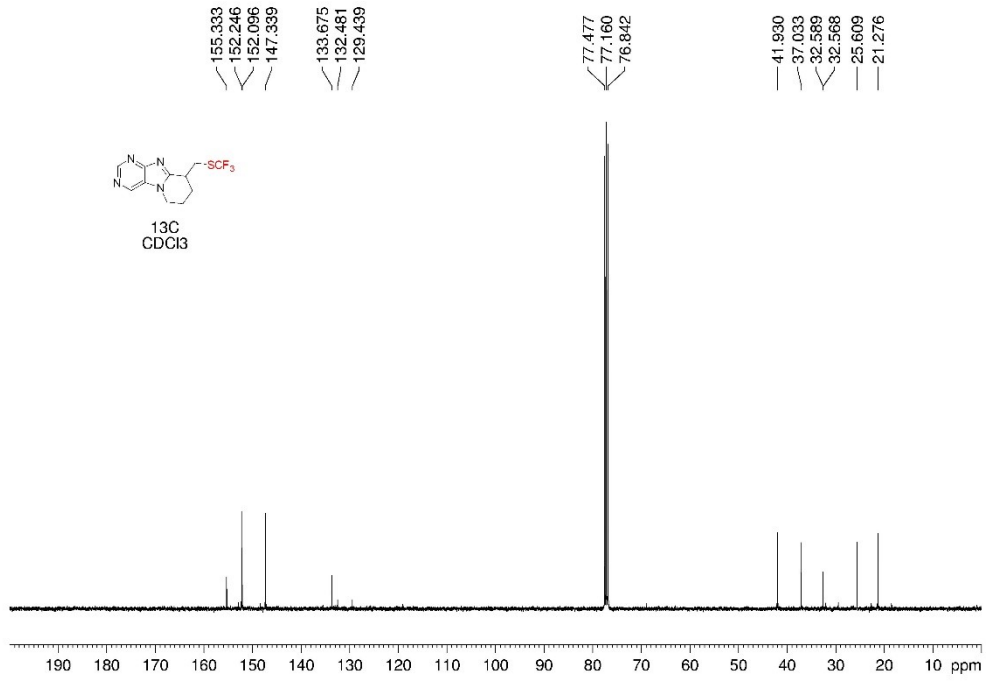



**Figure S64. $^{13}$C NMR (100 MHz, $CDCl_3$) of compound 3y**

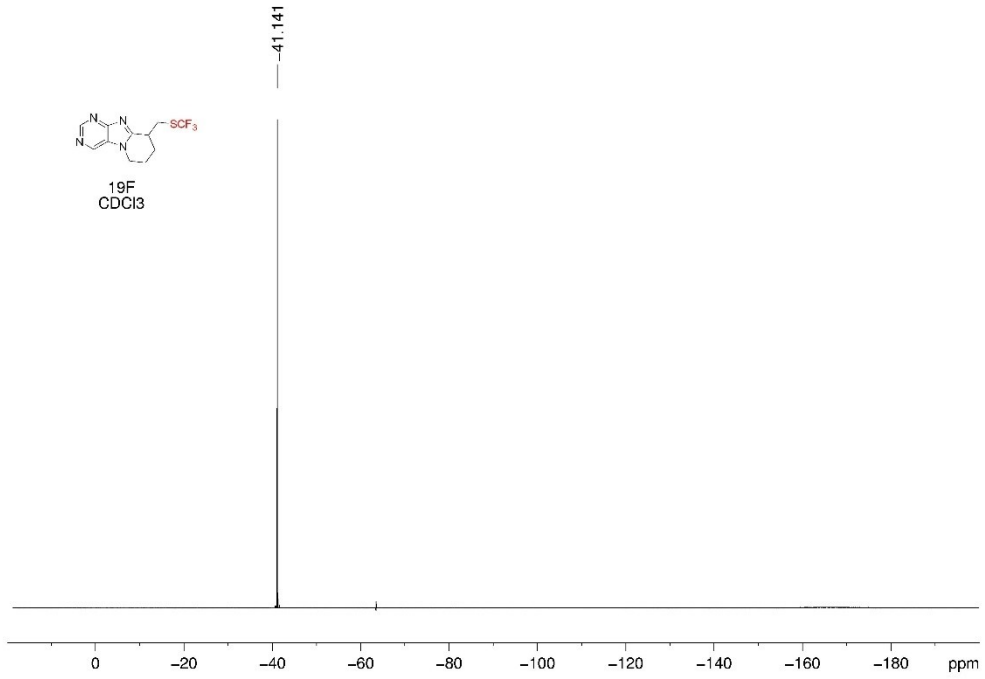



**Figure S65. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3y**

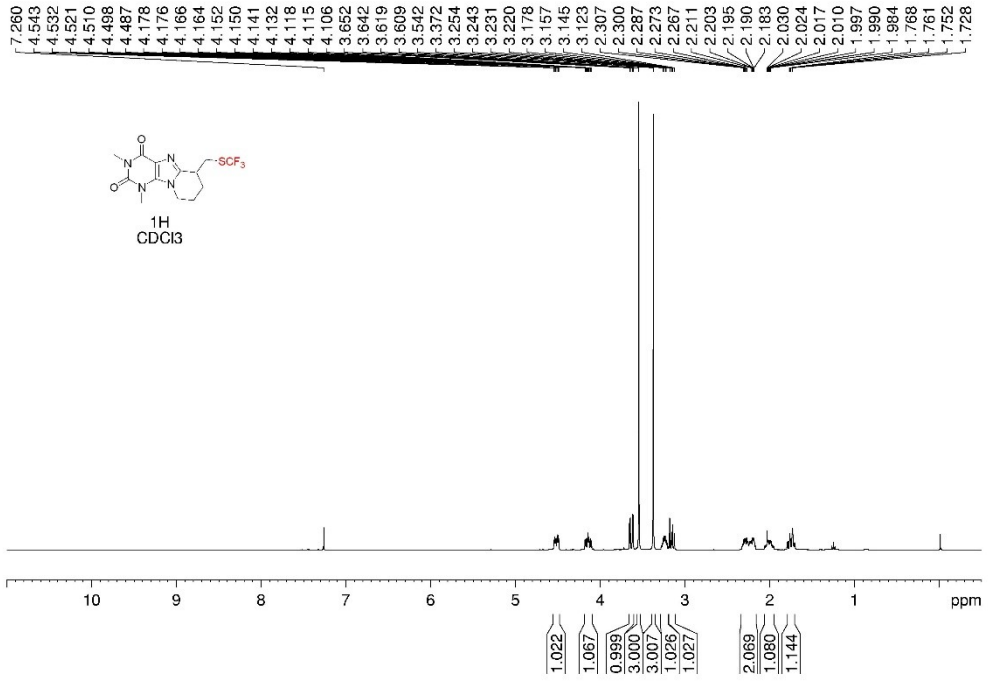



**Figure S66. $^{1}H$ NMR (400 MHz, $CDCl_3$) of compound 3z**

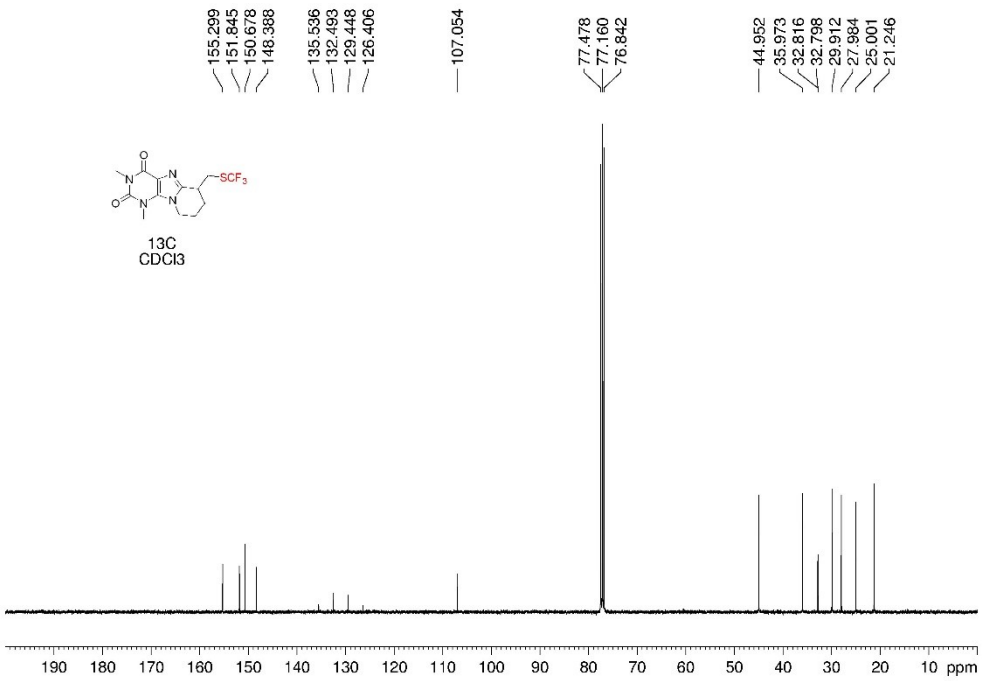



**Figure S67. $^{13}C$ NMR (100 MHz, $CDCl_3$) of compound 3z**

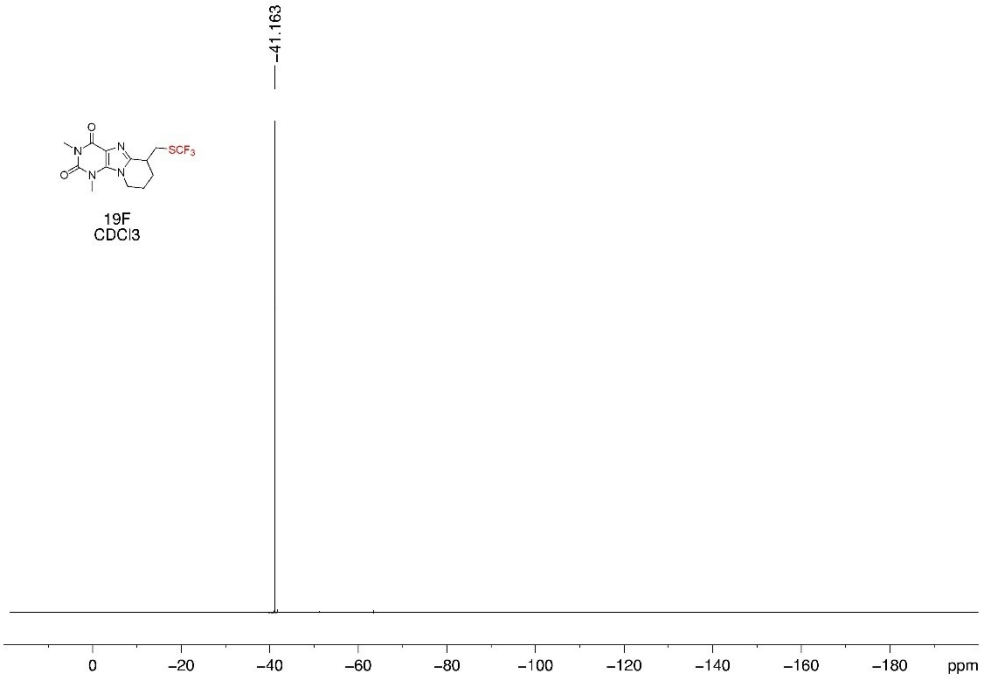



**Figure S68. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3z**

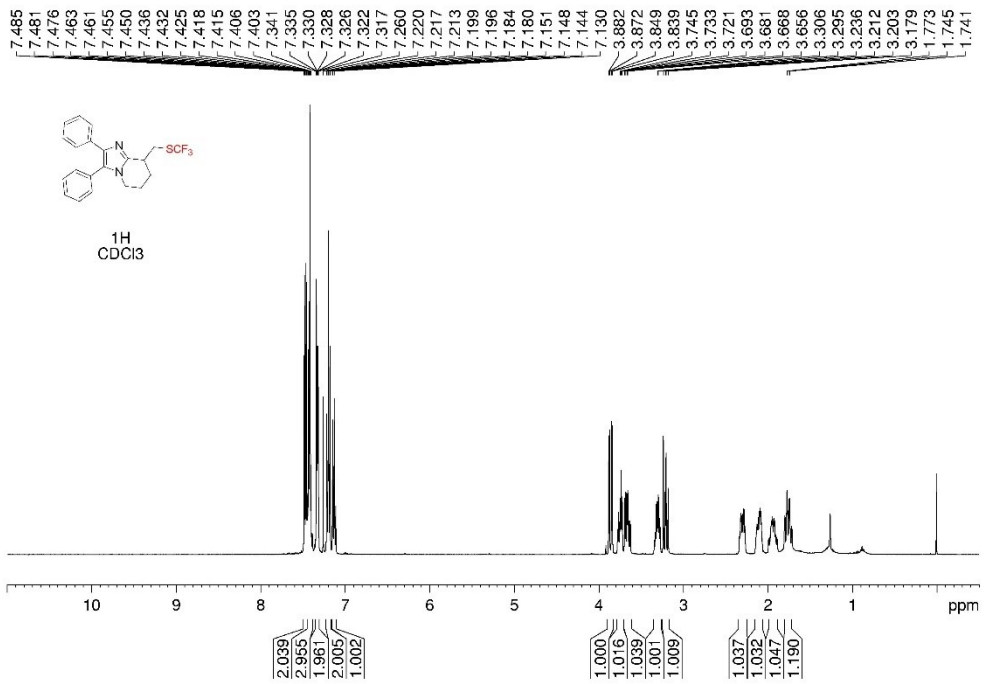



**Figure S69. $^{1}$H NMR (400 MHz, $CDCl_3$) of compound 3za**

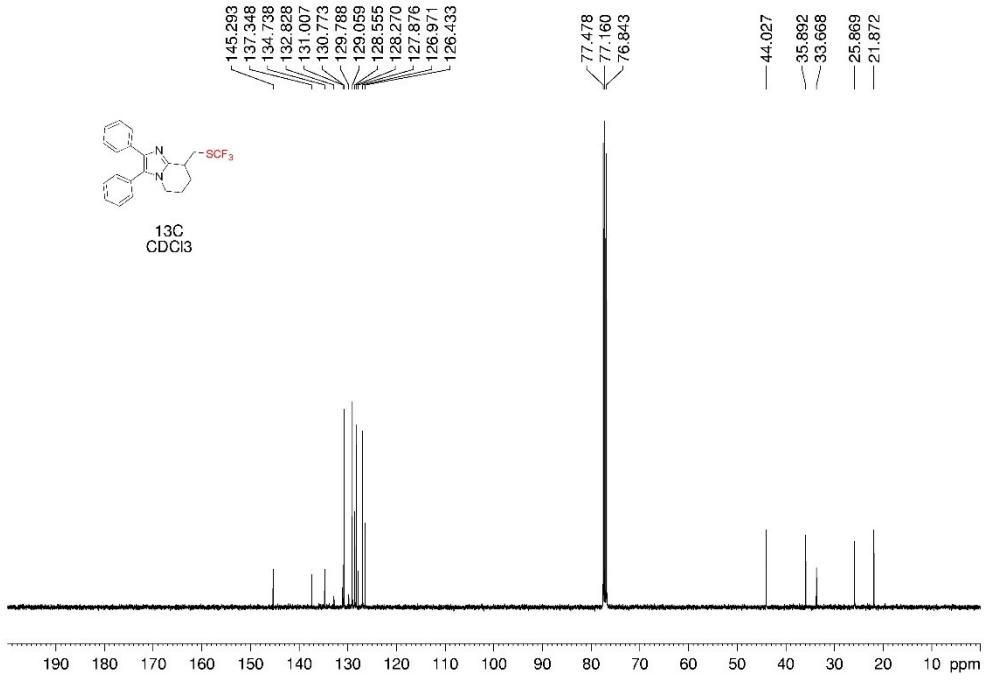



**Figure S70. $^{13}$C NMR (100 MHz, $CDCl_3$) of compound 3za**

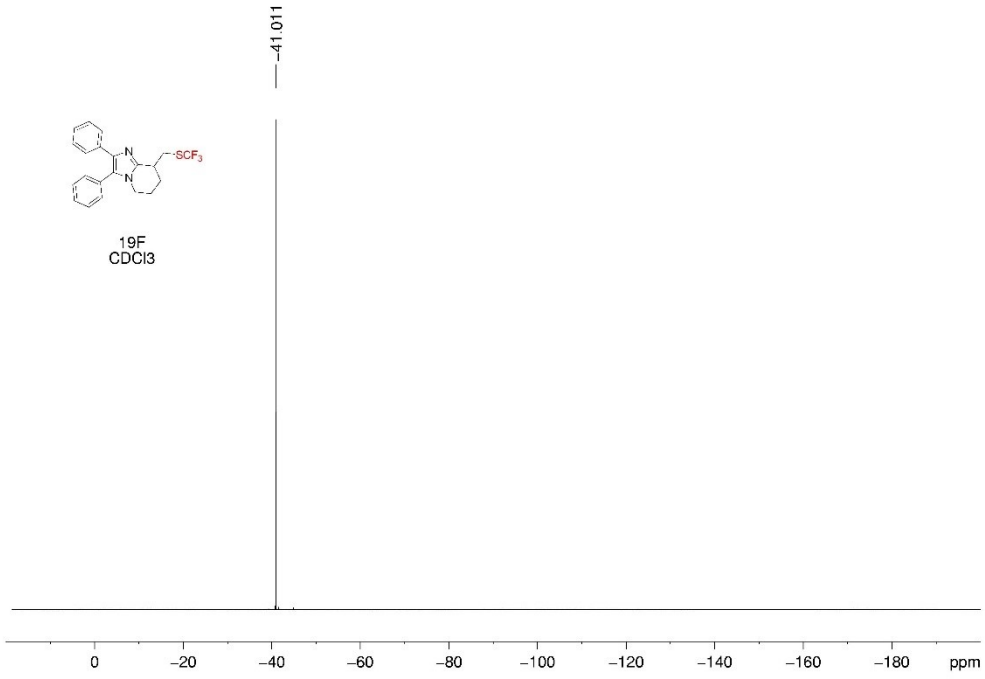



**Figure S71. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3za**

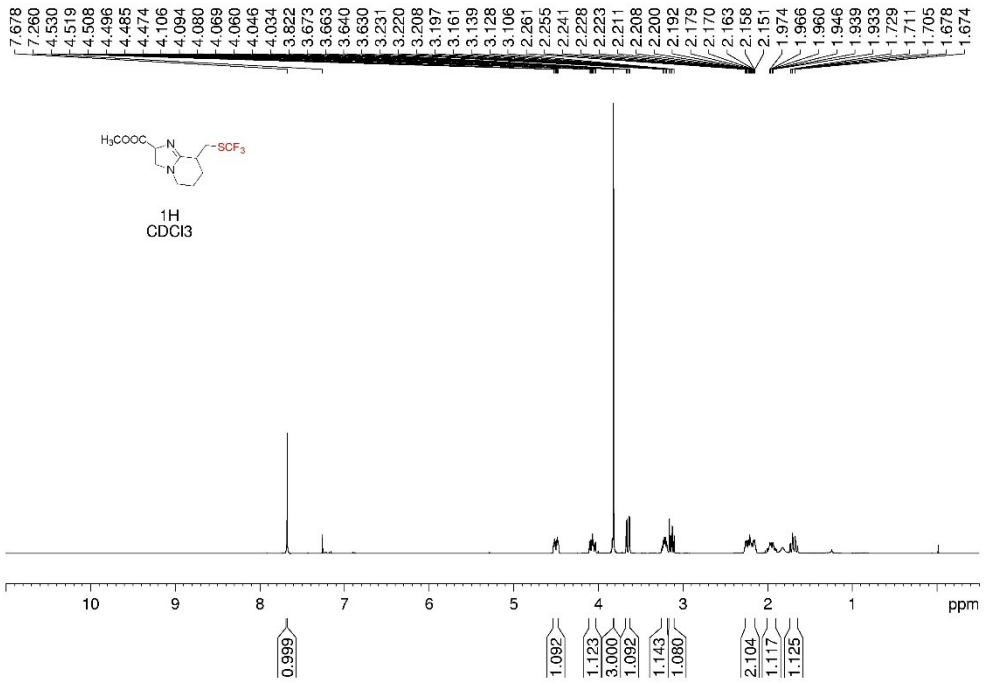



**Figure S72. $^{1}H$ NMR (400 MHz, $CDCl_3$) of compound 3zb**

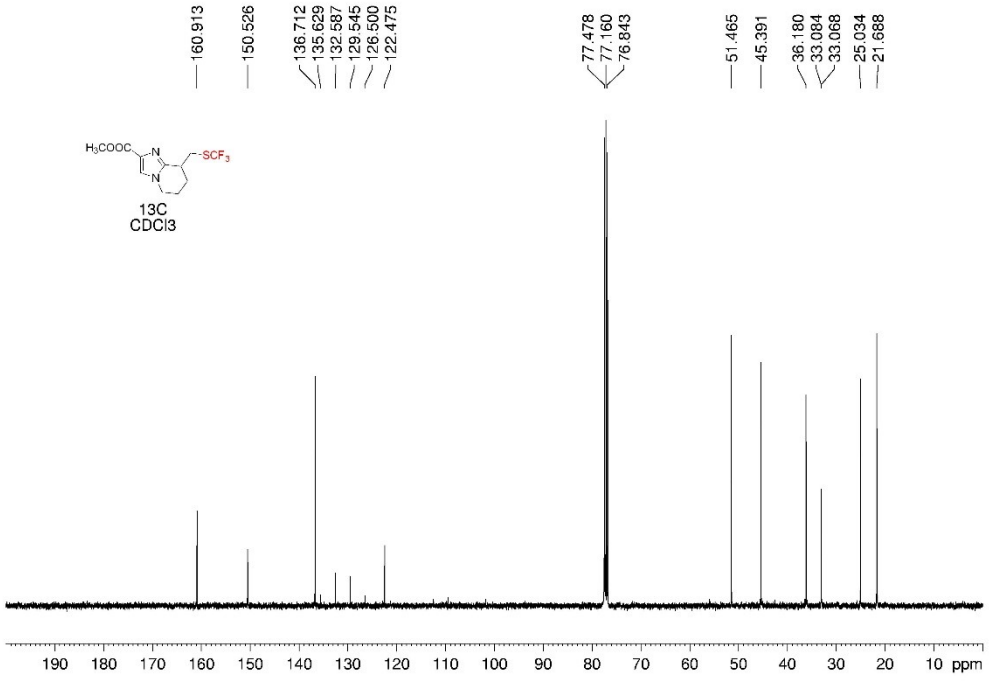



**Figure S73. $^{13}C$ NMR (100 MHz, $CDCl_3$) of compound 3zb**

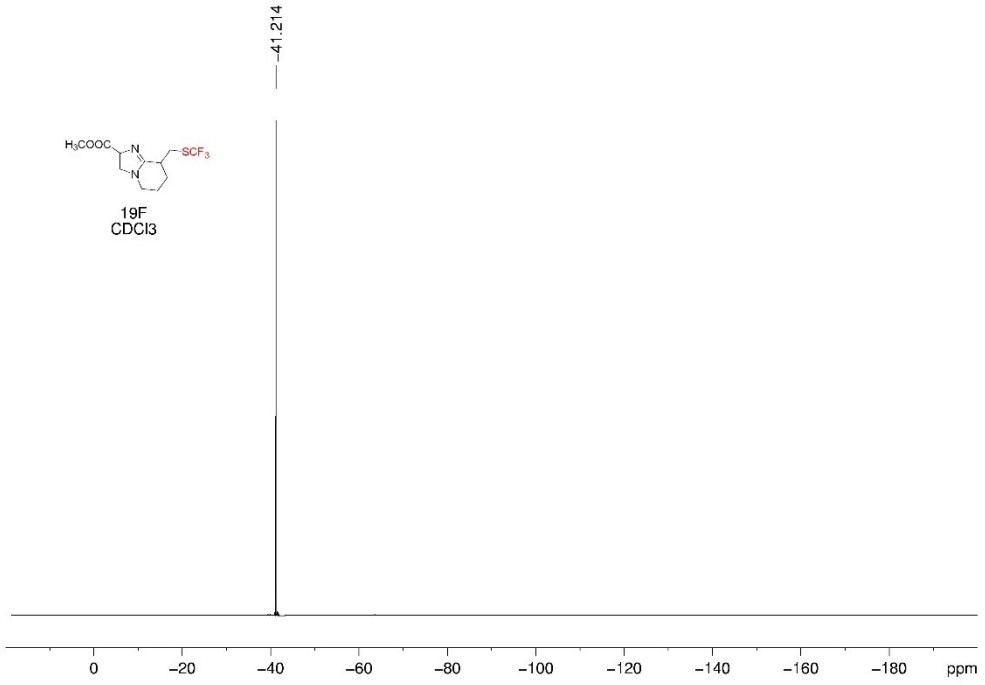



**Figure S74. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3zb**

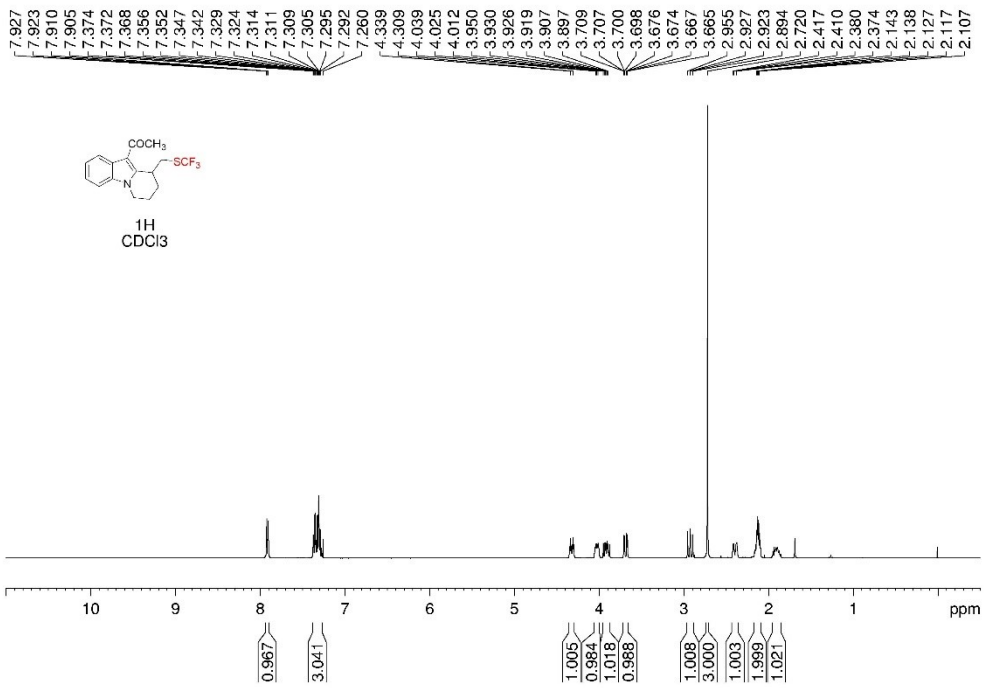



**Figure S75. $^{1}$H NMR (400 MHz, $CDCl_3$) of compound 3zd**

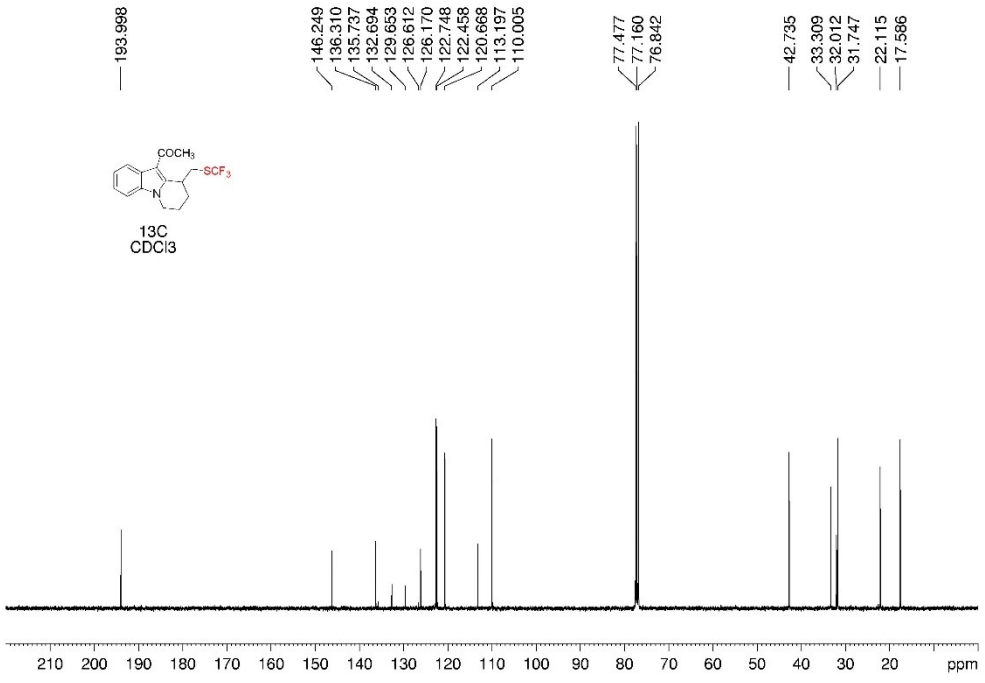



**Figure S76. $^{13}$C NMR (100 MHz, $CDCl_3$) of compound 3zd**

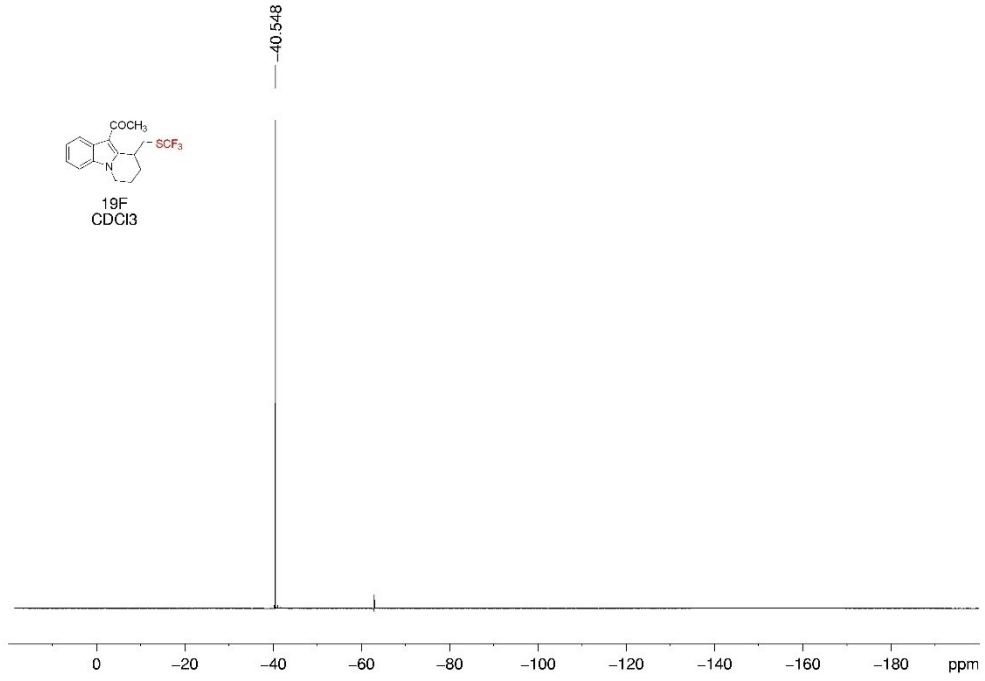



**Figure S77. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3zd**

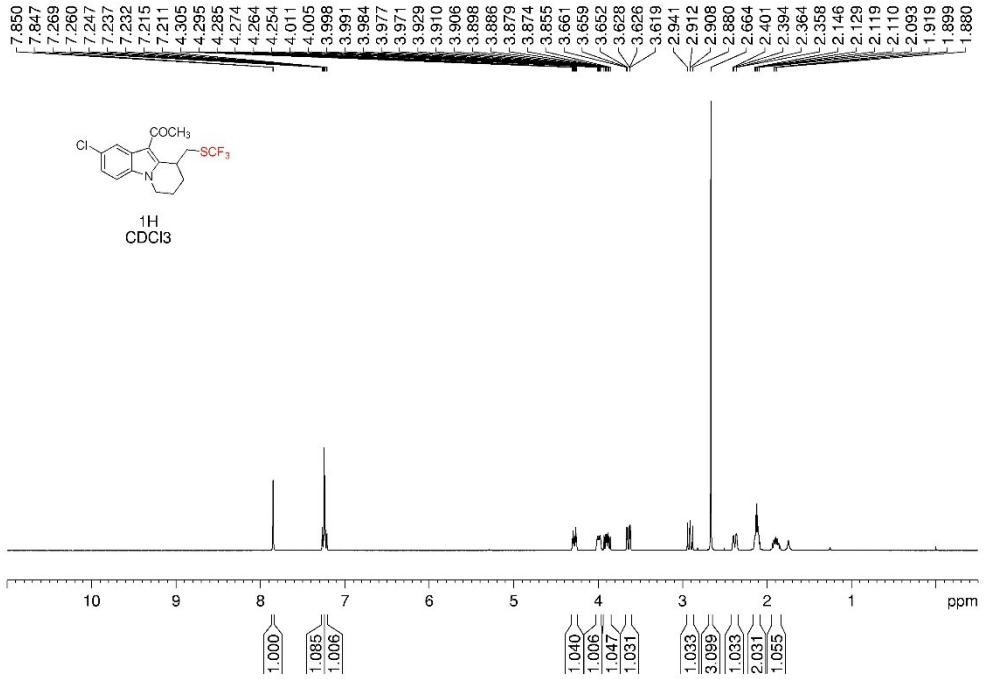



**Figure S78. $^{1}H$ NMR (400 MHz, $CDCl_3$) of compound 3ze**

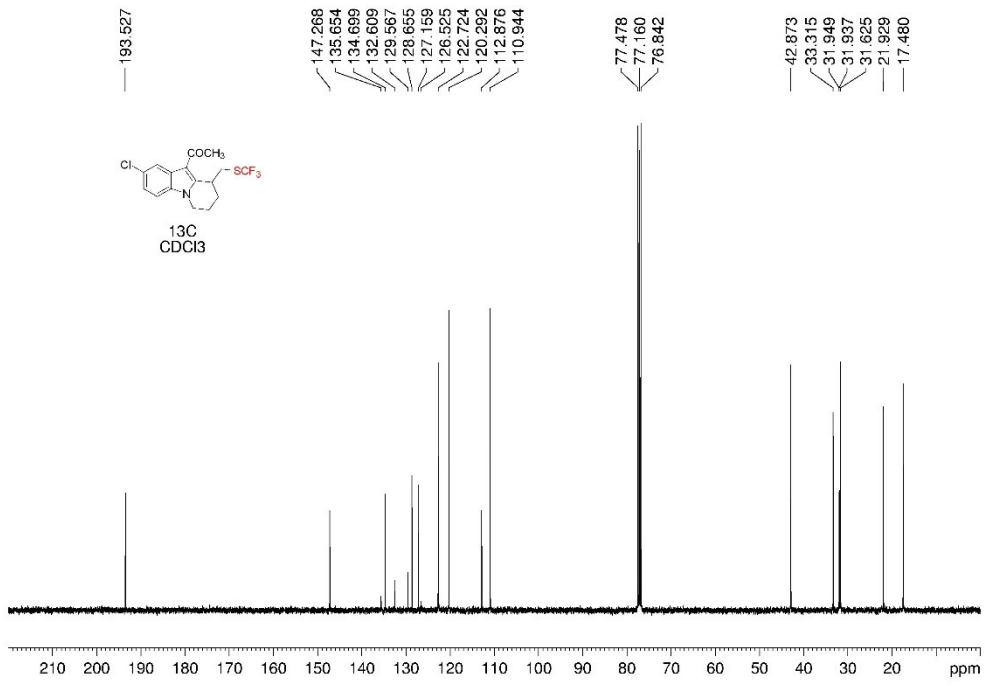



**Figure S79. $^{13}C$ NMR (100 MHz, $CDCl_3$) of compound 3ze**

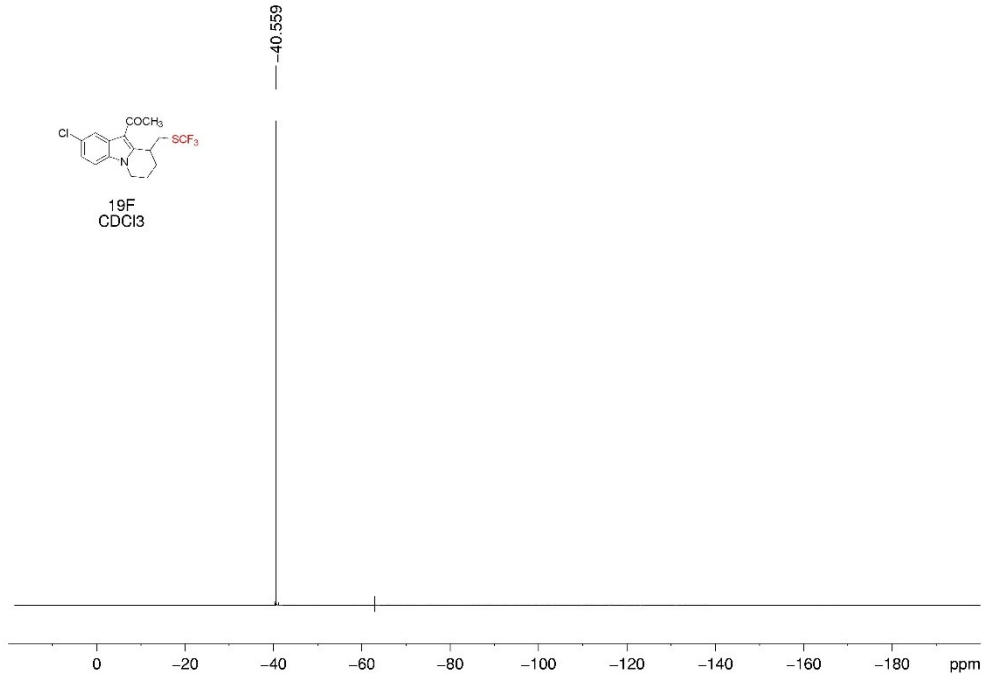



**Figure S80. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3ze**

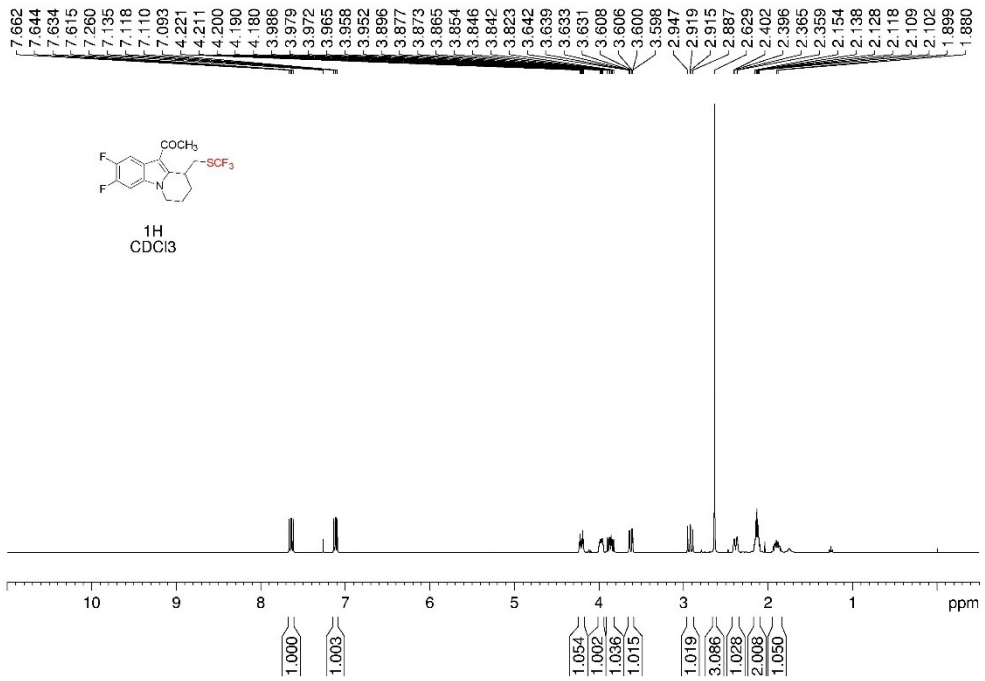



**Figure S81. $^{1}$H NMR (400 MHz, $CDCl_3$) of compound 3zf**

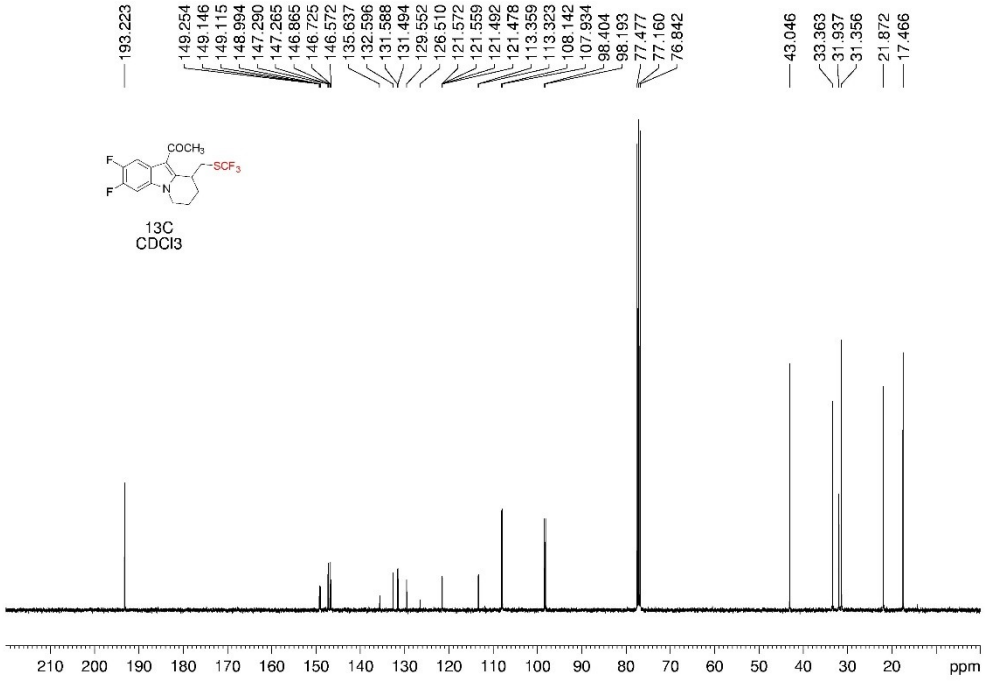



**Figure S82. $^{13}$C NMR (100 MHz, $CDCl_3$) of compound 3zf**

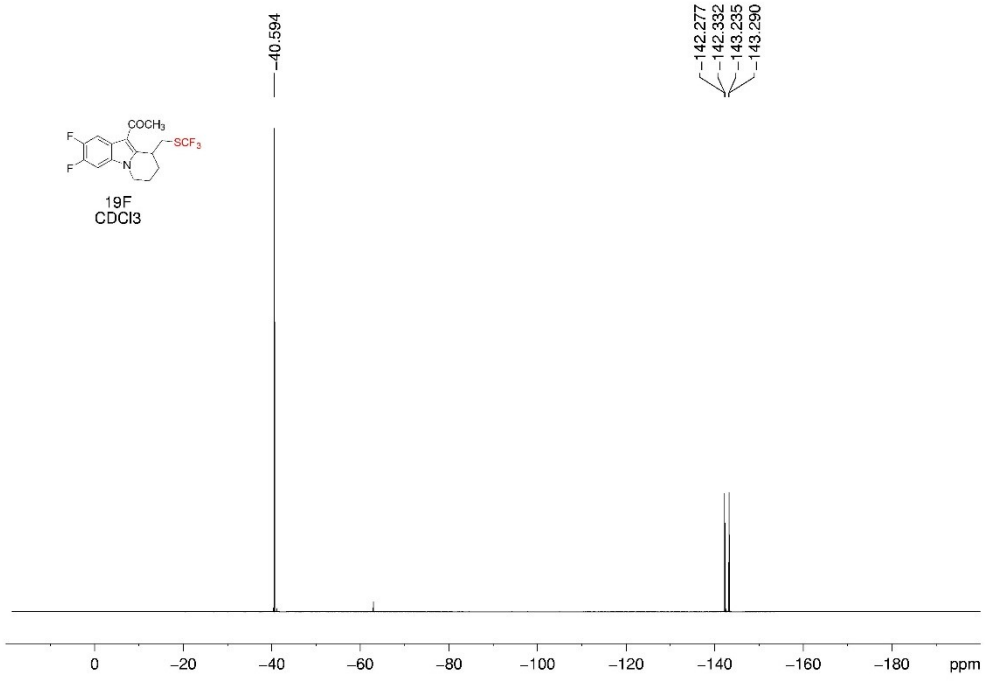



**Figure S83. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3zf**

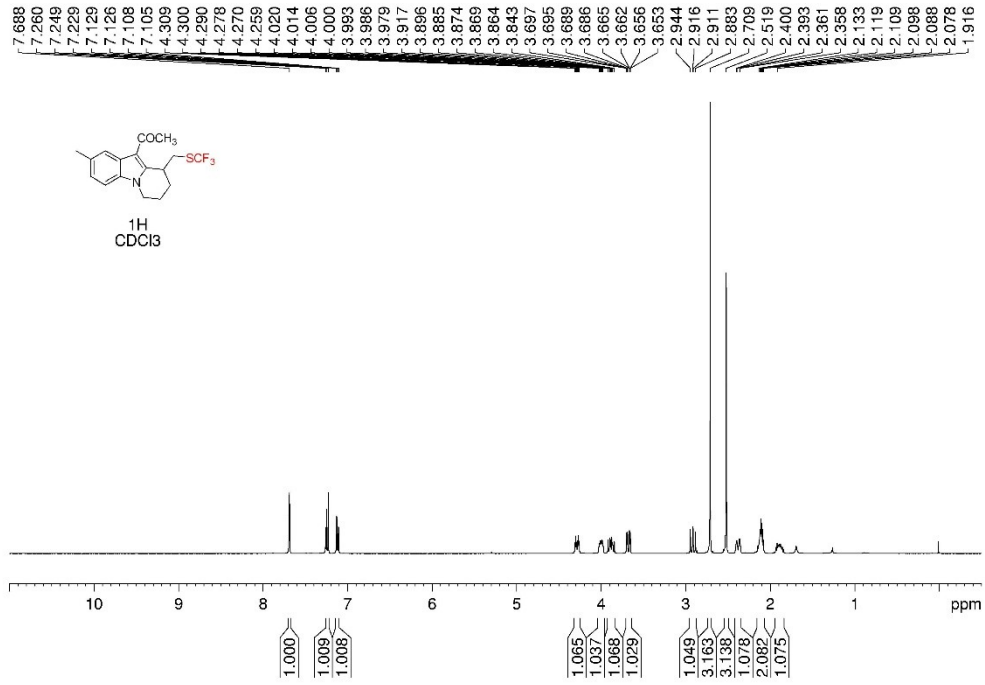



**Figure S84. $^{1}H$ NMR (400 MHz, $CDCl_3$) of compound 3zg**

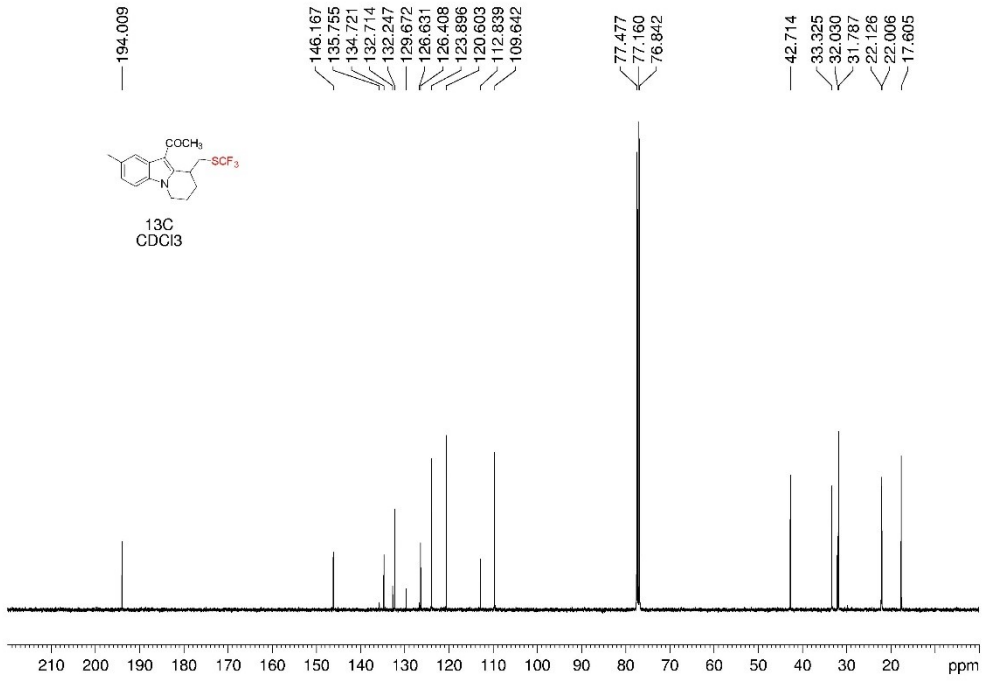



**Figure S85. $^{13}C$ NMR (100 MHz, $CDCl_3$) of compound 3zg**

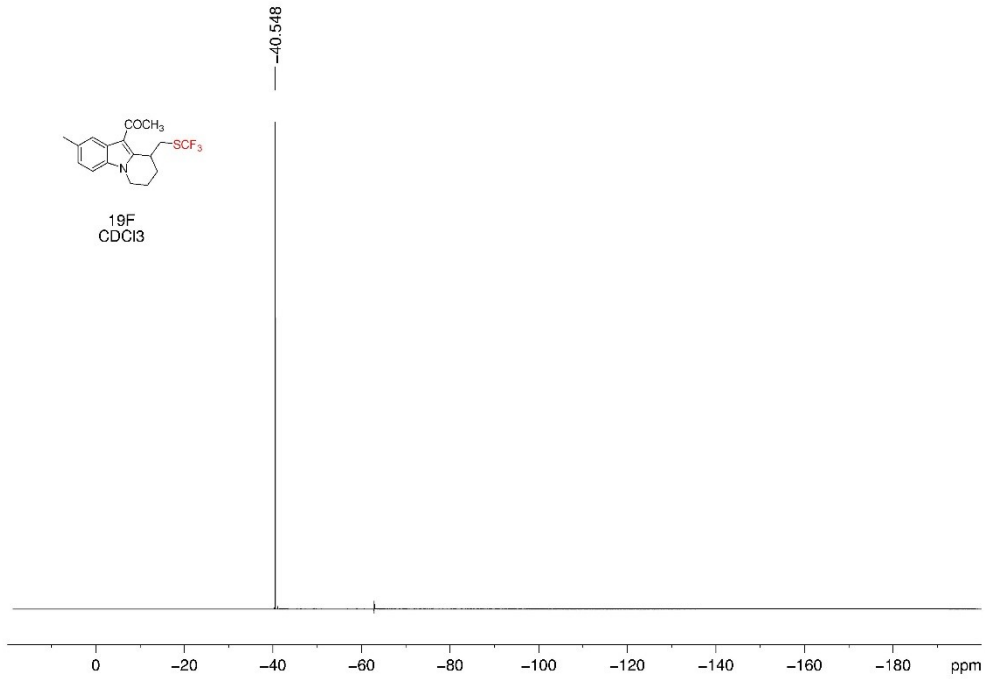



**Figure S86. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 3zg**

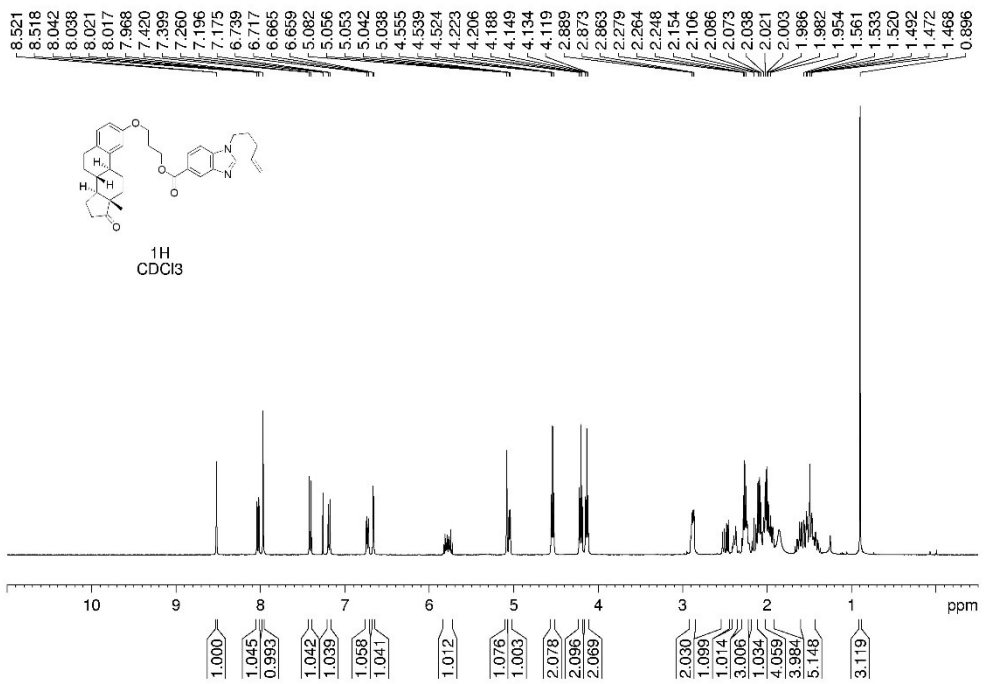



**Figure S87. $^{1}$H NMR (400 MHz, $CDCl_3$) of compound 6**

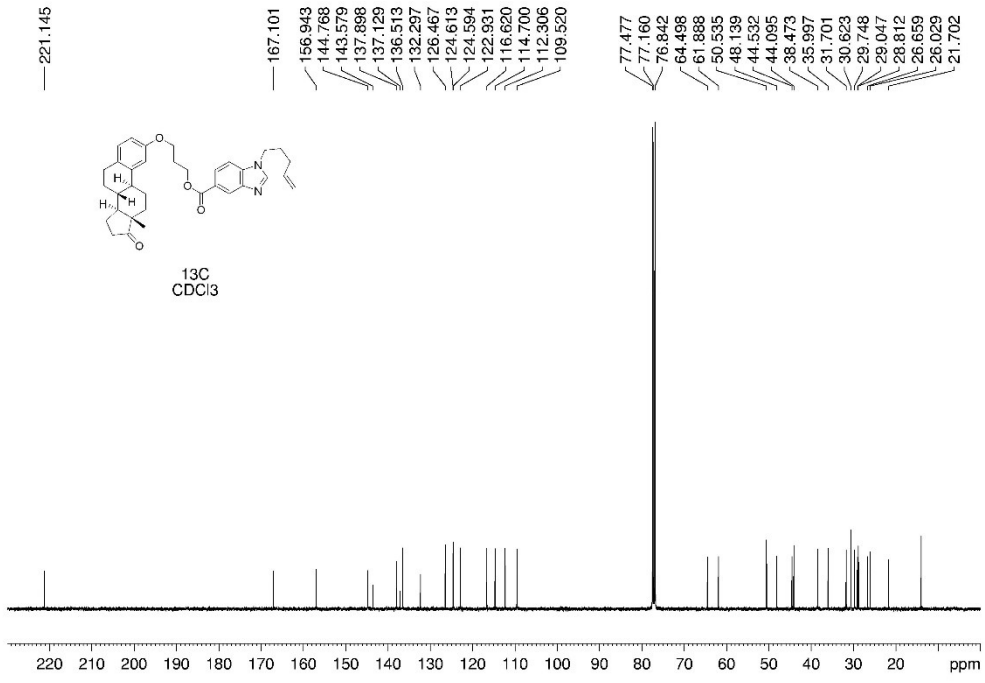



**Figure S88. $^{13}$C NMR (100 MHz, $CDCl_3$) of compound 6**

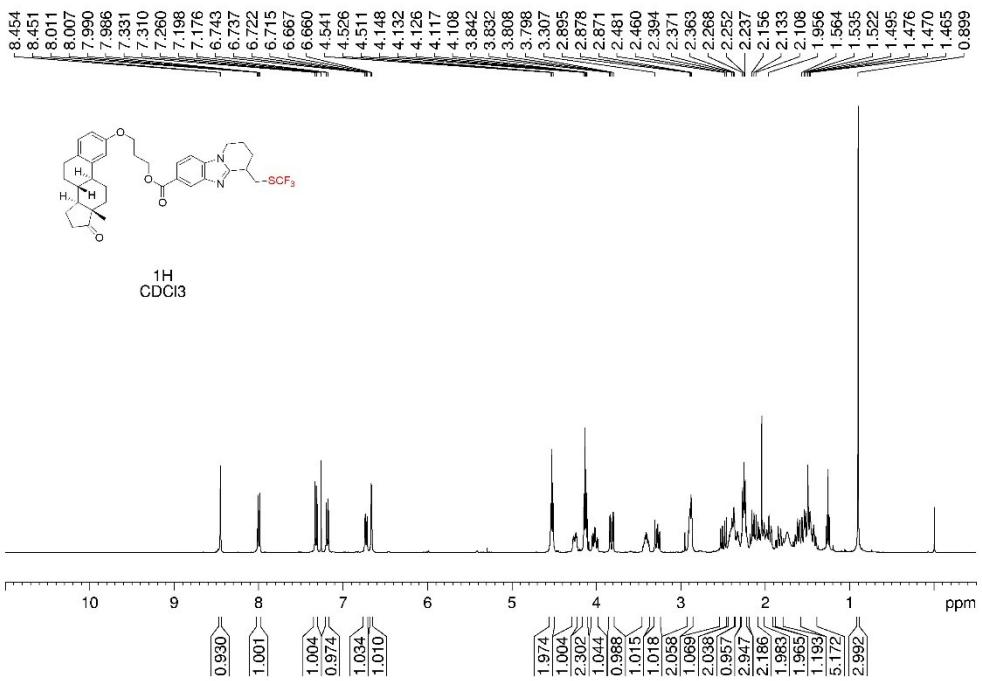



**Figure S89. $^{1}$H NMR (400 MHz, $CDCl_3$) of compound 7**

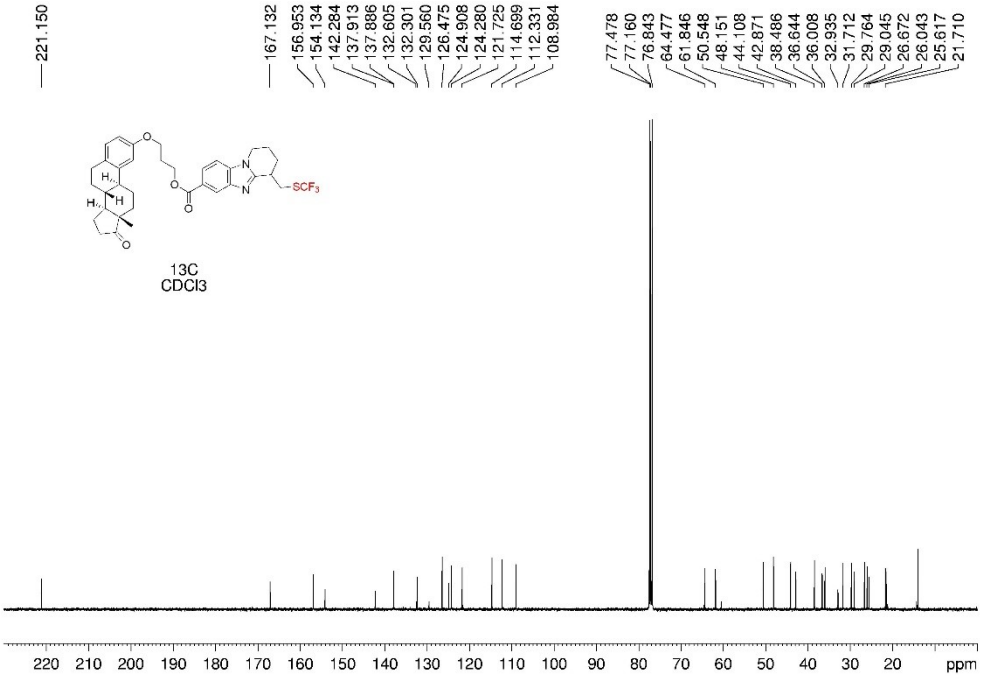



**Figure S90. $^{13}$C NMR (100 MHz, $CDCl_3$) of compound 7**

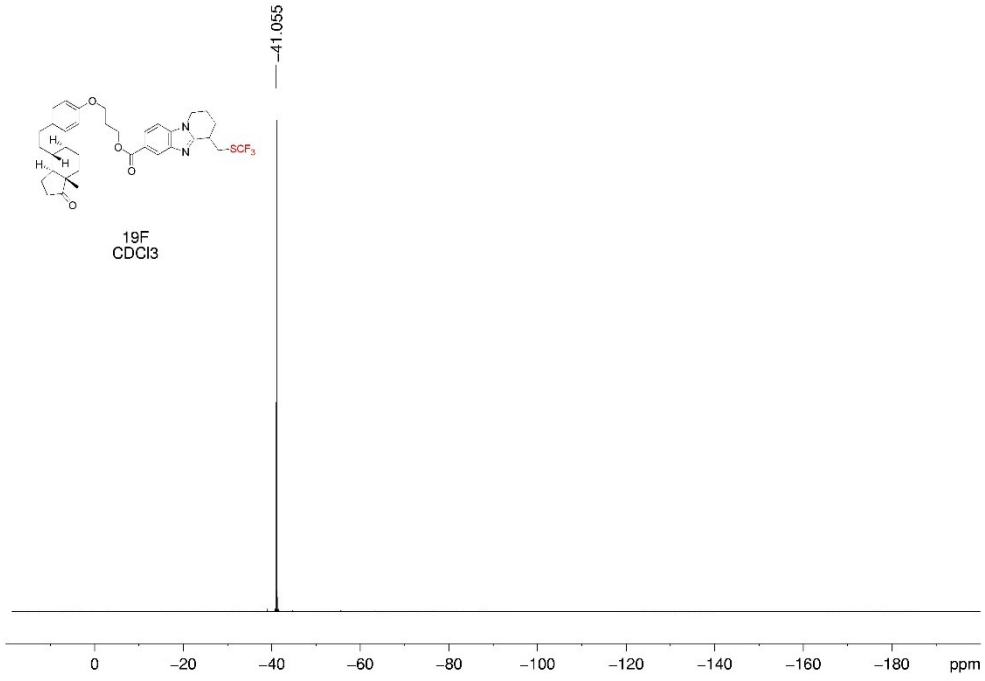



**Figure S91. $^{19}F$ NMR (376 MHz, $CDCl_3$) of compound 7**